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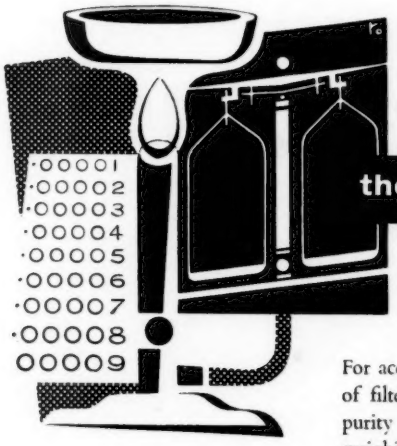

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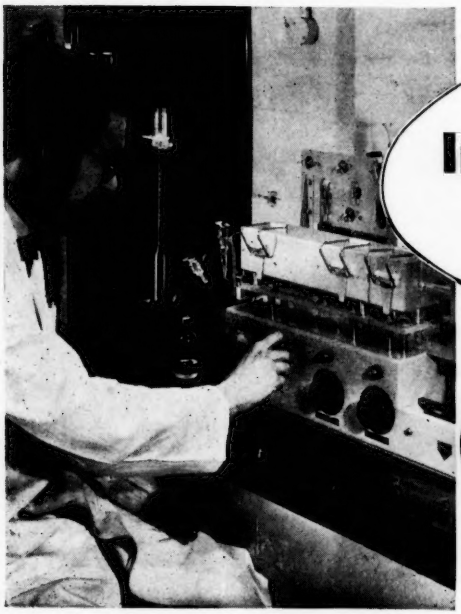

Incidental information

No. 11

items of interest from our laboratory notebooks

2-(2-Pyridyl)-imidazoline—is of interest to the theorist by reason of its structural relationship to 1:10—phenanthroline, and is of use to the practical analyst because of the selective reaction it affords for iron (*see* **Anal.Chem.,** 1954, **26,** 217.) It has lately been added to the Hopkin & Williams range under Code 7275.8.

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6-Aminothymol hydrochloride has been proposed quite recently (**Analyst.** 1957, **82,** 61) as a reagent for the colorimetric determination of thiamine in pharmaceutical and cereal products. The reagent is now available from Hopkin & Williams Limited (Hopkin & Williams Code 1395).

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***tri*-Sodium pentacyano-ammine ferroate** provides a means of determining isoquinoline (*see* **Analyst,** 1956, **81,** 718) in the presence of quinoline and quinaldine. But the reagent must be of suitable quality for such an application. Hopkin & Williams Code 7972 has been specially prepared and tested for this purpose.

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ANALYTICAL ABSTRACTS

1.—GENERAL ANALYTICAL CHEMISTRY

3820. **Density - composition tables for aqueous solutions of hydrochloric acid.** British Standards Inst. (2 Park St., London). B.S. 976: 1957, 32 pp.—The tables are re-published in their original form (B.S. 976: 1941) except that the data for conc. soln. at 20° have been supplemented by data at other temp. Appendices indicate the B.S. hydrometers available for use with the tables and methods of correction of hydrometer readings. N. E.

3821. **New substituted 2:2′-dipyridines [2:2′-dipyridyls] and their chelation as Fe^{2+} and Cu^{+} complex cations.** A. A. Schilt and G. F. Smith (Univ. of Illinois, Urbana, U.S.A.). *Anal. Chim. Acta*, 1957, **16** (5), 401–405.—4:4′-Diphenyl-2:2′-dipyridyl reacts with Fe^{2+} in the pH range 3·1 to 8·8 yielding a complex that is insol. in H_2O, sol. in ethanol and extractable from aq. ethanol with *iso*amyl alcohol. The complex has absorption max. at 552 and 386 mμ and $\epsilon = 21{,}300$ for both max. The Cu^{+} complex is too susceptible to oxidation for analytical purposes. 4:4′-Diamino-2:2′-dipyridyl yields a complex with Fe^{2+} at pH 4 to 14; it is soluble in aq. ethanol and is extracted by *iso*amyl alcohol. Absorption max. are shown at 379 mμ ($\epsilon = 13{,}640$) and 569 mμ ($\epsilon = 8135$). This reagent itself reduces Fe^{3+} to Fe^{2+}. The reactions of 4:4′:6:6′-tetramethyldipyridyl and of 6:4′:6″-triphenylterpyridyl are also described, but in less detail. W. C. Johnson

3822. **Certain properties of di-2-naphthylthiocarbazone and its bismuth and nickel complexes.** A. S. Grzhegorzhevskiĭ (Dnepropetrovsk Metallurgical Inst.). *Zhur. Anal. Khim.*, 1956, **11** (6), 689–693.—In CCl_4 soln., di-2-naphthylthiocarbazone (**I**) shows absorption max. at 665 and 450 mμ, and the molar absorption coeff. is 40,000. The value of the dissociation const., $2{\cdot}1 \times 10^{-13}$, is less than that for dithizone, 2×10^{-9}, showing that the bond between H and N is stronger. The complexes with Ni and Bi show absorption max. at ≃ 525 mμ and the molar absorption coeff. are 90,000 and 170,000, respectively, indicating that **I** is a more sensitive reagent than dithizone. The extraction const. of the complexes are also determined.

G. S. Smith

3823. **Analytical procedure with derivatives of acid - base indicators.** G. Schwarzenbach and R. Sallmann (CIBA Ltd.). U.S. Pat. 2,745,720 (May 15, 1956) (*cf.* Swiss Pat. 298,194, July 1, 1954).—Indicator dyes containing one or more substituents $R = CH_2N(CH_2COOH)_2$ in the *o*-position to phenolic hydroxyl groups are described for use in colorimetric and titrimetric determinations. The product 3:3″:5′:5″-tetrakis{[bis(carboxymethyl)amino]-methyl}phenolphthalein is of special interest.

Chem. Abstr.

3824. **Redox indicators in a heterogeneous phase and their analytical applications. I. General considerations.** F. Sierra Jimenez and F. Burriel-Martí (Anal. Chem. Lab., Fac. Sci., Madrid). *An. Real Soc. Esp. Fis. Quim.*, 1956, **52** (7–8), 459–468.—Numerous examples are given of "oxyadsorption" when unequal distribution of redox systems between the surface of the ppt. and the aq. phase occurs. The photo-activation of oxidation on the surface of the ppt. and the formation of metal ion - dye complexes are also discussed.

R. L. Mortlock

3825. **Analysis for industry [redox indicators].** R. Belcher. *Ind. Chem. Mfr*, 1957, **33**, 142–144; 198–200.—A survey is presented of the literature relating to the use of diphenylamine and its derivatives, *o*-phenanthroline, 2:2′-dipyridyl, and triphenylmethane dyestuffs as redox indicators with $KMnO_4$, $K_2Cr_2O_7$ and $Ce(SO_4)_2$ as titrants. (17 references.) S.C.I. Abstr.

3826. **Study of oxidation - reduction indicators. II. Ferroin as an oxidation - reduction indicator in micro-analysis.** L. M. Kul'berg and N. S. Frumina. *Uch. Zap. Saratovsk. Univ.*, 1956, **43**, 109–118; *Ref. Zhur., Khim.*, 1957, Abstr. No. 23,334.—A study has been made of ferroin as a redox indicator in the titration of dil. soln. of salts of Fe^{II} with dil. soln. (10^{-2}, 10^{-3} and 10^{-4} *N*) of strong oxidants [$K_2Cr_2O_7$, NH_4VO_3, $KMnO_4$ and $Ce(SO_4)_2$]. The results obtained are compared with those obtained with phenylanthranilic acid. The conditions for using ferroin in volumetric micro-analysis have been investigated (order of titrating, concn. and nature of mineral acids used, concn. of reagents, temp.).

C. D. Kopkin

3827. **Metallochromic indicators. II. 3:4-Dihydroxy-4′-nitroazobenzene and 3:4-dihydroxyazobenzene-4′-sulphonic acid as simple metallochromic models of catechol violet.** J. Körbl, E. Kraus, F. Jančík and R. Přibil (Res. Inst. Pharm. and Biochem., Prague, Czechoslovakia). *Chem. Listy*, 1957, **51** (2), 311–314.—A comparison of 3:4-dihydroxy-4′-nitroazobenzene (**I**) and 3:4-dihydroxyazobenzene-4′-sulphonic acid (**II**) with catechol violet (**III**) showed the behaviour of these new indicators towards various cations to be similar. **I** and **II** can therefore be characterised as metallochromic models of **III**. The suitability of **I** and **II** for chelatometric titrations with volumetric soln. of EDTA (disodium salt) was confirmed by the titration of various cations. Thus Bi^{3+} can be titrated (with **I** or **II** as indicator) in 0·1 *N* HNO_3 soln.; the colour change is yellow to red. An aq. soln. of $Th(NO_3)_4$ can also be determined with the use of the same indicators; a less sharp colour change (especially with **I**) was observed. Bivalent Cu can be titrated in strongly alkaline medium (4 ml of conc. aq. NH_3 and 4 ml of 0·5 *N* NaOH in 100 ml of H_2O), with **I** as indicator; the colour change is

red to blue. Calcium can be determined indirectly; when added in alkaline medium to a soln. of Cu-EDTA, an equiv. amount of Cu^{2+} is liberated and can be titrated with the use of **I** as indicator.
J. ZÝKA

3828. **Calcium hydroxide as a highly alkaline pH standard.** R. G. Bates, V. E. Bower and E. R. Smith. *J. Res. Nat. Bur. Stand.*, 1956, **56** (6), 305–312.—An excess of pure finely granulated $Ca(OH)_2$, made by heating well-washed low-alkali $CaCO_3$ to 1000° for 45 min., is shaken with water in a stoppered bottle at room temp., allowed to settle and filtered through a sintered glass funnel. It can be stored under water, diluted and filtered for use as required. The solubility varies inversely with temp., but no pptn. occurs up to 60°. The pH of a soln. satd. at 25° is 12·45. F. J. M.

3829. **Sodium carbonate as a volumetric standard.** W. C. Easterbrook (Res. Dept., I.C.I. Ltd., Nobel Div., Stevenston, Ayrshire, Gt. Britain). *Analyst*, 1957, **82**, 383–390.—Experiments made with a thermal balance on the prep. of Na_2CO_3 for use as a volumetric standard showed that heating the sesquicarbonate at 270° yields a product of satisfactory stability. A method by which high-grade $NaHCO_3$ is further purified and transformed into the sesquicarbonate before conversion into the normal carbonate by heating at 270° was finally adopted. Experiments include the assay of materials containing 100·023, 100·013 and 100·008% of Na_2CO_3. A recent spectrographic analysis of the ultimate standard silver, to which the Na_2CO_3 was referred, gave a value of rather better than 99·998% of Ag. A. O. JONES

3830. **Potassium tetraborate as a basic standard in acidimetry.** Ya. Ya. Sauka and Ya. K. Putnin' (Latvia State Univ., Riga). *Zhur. Anal. Khim.*, 1956, **11** (6), 668–671.—The use of $K_2B_4O_7.4H_2O$ as a standard for establishing the titre of acids is recommended. It is stable and its free moisture content, which can readily be removed by drying at 65°, is $\simeq$ 0·04%. Its solubility at 20° is 18·5 g per 100 g of water and at 60° is 58·6 g per 100 g.
G. S. SMITH

3831. **Electrochemical behaviour of electrodes in potentiometric titrations with Trilon B [EDTA, disodium salt].** B. N. Kabanov and L. Ya. Polyak. *Zhur. Anal. Khim.*, 1956, **11** (6), 678–685.—With Pt as reference electrode and W as indicator electrode the latter is polarised anodically during titration with EDTA in ammoniacal soln. It is supposed that EDTA molecules adsorbed on the surface of the electrode dislodge O and cause thereby the potential to become more negative. With Mo as indicator electrode, EDTA lowers the overvoltage for the anodic oxidation of Mo, but it has no effect on the cathodic process of ionisation of O. G. S. SMITH

3832. **Semi-automatic subtraction of titration curves. Versatile curve-plotting device.** V. L. Stevens and E. L. Duggan (Univ. of California, Berkeley, U.S.A.). *Anal. Chem.*, 1957, **29** (7), 1073–1076.—All numerical records are eliminated by using a simple plotting device which employs a slide-wire for converting distances into d.c. voltages. This can be used for the routine subtraction of titration curves to yield the difference curve. The corrected titration curve is immediately plotted, point by point, on a chart recorder. The apparatus could be used for curve subtraction in spectrophotometry. K. A. PROCTOR

3833. **Method of improving the null-point of thermal conductivity cells for gas-liquid chromatography.** W. F. Madden, R. K. Quigg and C. Kemball (Dept. of Chem., The Queen's Univ. of Belfast, N.I.). *Chem. & Ind.*, 1957, (26), 892.—The persistent residual balance potential which makes a purely resistive balance unobtainable with thermal conductivity cells and a.c. has been investigated. This condition, forecast by Patchett's equation, is remedied by the inclusion of a filter in the amplifier and capacity in the bridge. Choice of these and experiments with higher frequency are discussed. E. G. CUMMINS

3834. **Vapour-phase chromatography and the telegrapher's equation.** M. J. E. Golay (Perkin-Elmer Corp., Norwalk, Conn., U.S.A.). *Anal. Chem.*, 1957, **29** (6), 928–932.—A mathematical theory of kinetics of gas chromatography is developed by comparing the fractionating column with an electrical transmission line. Several conclusions, such as the existence of an optimum flow rate of carrier gas for max. band separation, are derived from the simple theory established.
K. A. PROCTOR

3835. **Elution time and resolution in vapour chromatography.** A. K. Wiebe (Hercules Powder Co., Wilmington, Del., U.S.A.). *J. Phys. Chem.*, 1956, **60**, 685–688.—Some of the variables associated with vapour-phase chromatography were studied to determine the conditions for min. elution time and max. resolution. The elution time varied inversely as the carrier-gas flow rate, directly as the column length, and exponentially with the reciprocal of the absolute temp. An equation relating these variables to the free energy was derived. Resolving power was improved with increase in column length and decrease in column temp., but passed through a max. with increasing carrier-gas flow rate. The improvement in resolution did not, however, appear to vary linearly with column length. The resolving power of the column reaches a point beyond which small improvements are obtained with comparatively large increases in elution time and with considerable dilution in the carrier gas. A definition of column efficiency was suggested which relates the resolving power directly with the partition coeff. for all compounds and with the v.p. for all classes of similar compounds.
CHEM. ABSTR.

3836. **Katharometric measurement of theoretical plate numbers in gas chromatography.** J. Bohemen and J. H. Purnell (Dept. of Phys. Chem., Cambridge). *Chem. & Ind.*, 1957, (25), 815–817.—The importance of the determination of theoretical plate numbers (N) at several different filament temperatures to confirm constancy is stressed. Katharometric work with N or CO_2 as carrier gases and both non-polar and polar materials such as *n*-heptane, hept-1-ene, *cyclo*hexane and *n*-butyl methyl ether has been found to be subject to large variations in N undetectable from the peak shape or other information. E. G. CUMMINS

3837. **Use of silica gel and alumina in gas-adsorption chromatography.** S. A. Greene and H. Pust (Aerojet-General Corp., Azusa, Calif., U.S.A.). *Anal. Chem.*, 1957, **29** (7), 1055.—The resolution of a mixture of low-boiling gases and some hydro-

carbons on silica gel and alumina is compared, with 70 ml per min. of He as carrier gas and a column of 20 ft. of 20 to 40-mesh adsorbent, in the apparatus previously described (Greene *et al.*, *Anal. Chem.*, 1956, **28**, 1369). With silica gel, good resolution of lower-boiling but unsatisfactory separation of higher-boiling components was obtained. Alumina resolved all components except CO_2. Air is not separated by either. It is suggested that when resolution of air into O and N is not required, silica gel could be used for separations usually carried out on charcoal. R. E. ESSERY

3838. **A useful method for the pretreatment of potassium bromide when used as an embedding medium in i.r. spectroscopy.** H. von Dietrich (Chem. Inst. Univ. Heidelberg, Germany). *Z. Naturf.*, 1956, **11b** (3), 175-176.—The advantages of KBr as an embedding medium are to some extent nullified by the presence of moisture, which causes a line at 2·9 μ and 6·1 μ. To remove this water the following procedure has been adopted. Melted KBr is poured into a vessel which is cooled externally. Rapid solidification gives a vitreous crust showing few cracks. When coarsely powdered it compresses at low pressure into clear tablets of excellent i.r. transmission. The powdered KBr shows no changes after storage at room temperature for 6 months and reveals no traces of moisture. E. KAWERAU

3839. **Practical application of colorimetry in industrial laboratories.** F. Braun (Univ. Catholique, Louvain). *Peint.-Pigm.-Vern.*, 1956, **32** (9), 750–756.—Systems of colorimetry have found little application in industry because of the involved theory, confused nomenclature and the absence of suitable apparatus. The measurement of colour by the bichromatic co-ordinate system by Hunter is rapid and not unduly complicated. With the apparatus described, it is possible to measure the type of colour, its depth (its mixture with white, grey or black) and the colour intensity with or without spectral reflection. Colour differences of two different samples whether transparent or opaque may be estimated, and the fluorescence of optical bleaches may be evaluated with additional apparatus and a Wood's lamp. F. J. M.

3840. **Studies on polarographic analysis. XXIV. Use of double complexing agents as supporting electrolyte. (2). The EDTA - KCN base solution.** Masayoshi Ishibashi, Taitiro Fujinaga and Masanori Sato. *Bull. Inst. Chem. Res., Kyoto Univ.*, 1956, **34** (1–2), 10–19 (in English).—This paper has been published, in Japanese, in *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1956, **77** (5), 696. (*Cf. Anal. Abstr.*, 1957, **4**, 357.) F. J. M.

3841. **Interaction of β-particles with matter.** R. H. Müller (Los Alamos Sci. Lab., N.M., U.S.A.). *Anal. Chem.*, 1957, **29** (6), 969–975.—A study of the relative back-scattering of β-particles from matter shows simple regularities for all elements and compounds, and these can be measured with high precision. The values predicted for pure crystalline solids can be checked to a precision close to that with which the atomic weights are known. Measurements can be applied to solids, liquids and soln. K. A. PROCTOR

2.—INORGANIC ANALYSIS

3842. **Removal of inclusions for analysis by an ultrasonic "jack hammer".** G. L. Kehl, H. Steinmetz and W. J. McGonnagle (School of Mines, Columbia Univ., New York). *Metallurgia, Manchr*, 1957, **55**, 151–154.—A technique is described for the removal of inclusions of min. diameter $\simeq 10$ μ by means of a pointed stylus oscillating at ultrasonic frequencies. S.C.I. ABSTR.

3843. **Inorganic paper chromatography. XXVI. The separation and detection of the constituents of some alloys.** Shiro Harasawa and Hiroshi Aihara (Fac. of Engng, Yamaguchi Univ., Ube, Yamaguchi Prefecture). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1957, **78** (3), 400–404.—The paper-chromatographic separation of Cr, Fe and Ni in nichrome is effected by the use of a mixture of satd. ethanolic soln. of dimethylglyoxime, conc. HCl and *iso*amyl alcohol (10 + 3 + 3). The R_F values are 0·80, 0·45 and $\simeq$ 0·1 for Fe^{3+}, Ni^{2+} and Cr^{3+}, respectively. Components of brass (Cu, Zn and Pb) are satisfactorily separated by development with a mixture of amyl alcohol and HCl (10 + 3). For the qual. analysis of cupro-nickel, the use of a mixture of ether, acetic acid and conc. HCl (10 + 8 + 3) is recommended, the R_F values of Fe, Cu, Mn and Ni being 0·8, 0·45, 0·22 and $<$ 0·1, respectively. The same developer is also used for the qual. analysis of aluminium brass; the R_F values are 0·8, 0·7, 0·45, 0·22 and $<$ 0·05 for Fe, Zn, Cu, Mn and Al, respectively; spraying with benzidine in acetic acid was used for the detection of Mn ($\simeq$ 0·1 %). K. SAITO

3844. **Spectrographic analysis of gases at pressures close to atmospheric.** O. P. Bochkova and E. Ya. Shreĭder. *Vestn. Leningr. Univ.*, 1956, (16), 57–63; *Ref. Zhur., Khim.*, 1957, Abstr. No. 23,494.—The determination of Ne, He and A in air is carried out by excitation of the spectra in a high-voltage condensed spark discharge. The line-pairs used analytically are Ne 5876 - C 5880, A 4880 - O 4871 and He 5876 - C 5880 A. The sensitivity of the determination is 0·1%, and the probable error is 5 to 8%. C. D. KOPKIN

3845. **Determination of small quantities of water by the Karl Fischer method.** E. P. Bahari (Birmingham Univ.). *Birmingham Univ. Chem. Engr*, 1956, **7**, 70–79.—Two different types of apparatus based on the Karl Fischer titration method and the "dead-stop" end-point technique are described. One, a double-burette apparatus, was used for samples containing 0·01% to 10% of H_2O; the other, an automatic titrator, was used for micro-determination of samples with 0·002% to 0·01% of H_2O. A technique for the exclusion of atm. moisture during the manipulation of samples is also described. CHEM. ABSTR.

3846. **Application of thermistor bridge method to determination of water in solids.** R. M. Engelbrecht and S. Drexler (Monsanto Chem. Co., El Dorado, Ark., U.S.A.). *Anal. Chem.*, 1957, **29** (7), 1100–1101.—Moisture is removed from NH_4NO_3 with a stream of dry N and determined by the thermistor bridge - calcium hydride method. The time for analysis is 6 to 10 min., and the necessary apparatus is easily and cheaply assembled. K. A. PROCTOR

3847. **A simple method for the assay of tritium in water samples.** J. E. S. Bradley and D. J. Bush (Postgrad. Med. School, London, England). *Intern. J. Appl. Radiation and Isotopes*, 1956, **1**, 233–234.—Addition of acetone to tritiated H_2O increases the H content of the counting mixture without losing the advantages of utilising water directly. The exchange H_2O - acetone is very rapid in the presence of alkali. It presumably takes place via the keto - enol tautomerism, involving a mesomeric anion. CHEM. ABSTR.

3848. **Determination of hydrogen peroxide in the presence of oxalic acid.** J. Bitskei (Inst. Inorg. Chem., Tech. Univ., Budapest). *Acta Chim. Acad. Sci. Hung.*, 1957, **10** (4), 327–333 (in German).—Excess of 0·1 *N* NaOCl is added to the sample. When the reaction is completed, an equiv. quantity of 0·1 *N* $Na_2S_2O_3$ is added and the excess titrated with NaOCl. Brazilin (1% ethanolic soln.) is used as indicator and KI (5% soln.) as catalyst. The colour change at the end-point is from red - violet to yellow - green. The oxalic acid can then be determined on the same sample by titration with $KMnO_4$, after acidification. G. BURGER

3849. **Determination of nitrate and chloride in sodium hydroxide solutions by means of cation exchangers, in the manufacturing control of alkaline batteries.** G. Gabrielson and B. Andersson (AB Tudor, Nol, Sweden). *Anal. Chim. Acta*, 1957, **16** (5), 425–427.—Sodium hydroxide soln., used for converting $Ni(NO_3)_2$ into $Ni(OH)_2$ and $CdCl_2$ into $Cd(OH)_2$ in battery plates, is controlled for NO_3^- or Cl^- content by diluting it to $\simeq N$ strength, passing it through Amberlite IR-120 cation-exchange resin (H form) and titrating the residual acidity with 0·1 *N* NaOH. W. C. JOHNSON

3850. **Determination of traces of potassium in reagent chemicals by sodium tetraphenylboron and sodium cobaltinitrite.** W. K. Kingsley, G. E. Wolf and W. E. Wolfram (J. T. Baker Chem. Co., Phillipsburg, N.J., U.S.A.). *Anal. Chem.*, 1957, **29** (6), 939–941.—The gravimetric tetraphenylboron and the gravimetric and turbidimetric cobaltinitrite methods of determining K in reagents, especially in sodium compounds, are compared with each other and with the flame-photometric methods. In particular, the presence of Na^+ gives high results with the cobaltinitrite method, but has little effect on results in the tetraphenylboron procedure; in addition, Fe^{3+}, Al^{3+}, Ca^{2+}, Mg^{2+}, Cu^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, SO_4^{2-} and PO_4^{3-} do not interfere in the second method and its results agree more closely with those of flame photometry. D. A. PANTONY

3851. **Determination of potassium in rocks and minerals by flame photometry.** I. G. Gurvich and E. I. Khanaev. *Izv. Akad. Nauk SSSR, Ser. Geol.*, 1956, (6), 101–109; *Ref. Zhur., Khim.*, 1957, Abstr. No. 23,392.—A detailed description of the instrument and appurtenances is given. The influence of Na, Ca, Mg, Ba, Sr and Li on the intensity of the K lines is studied. The greatest influence is shown by Na and Mg, that of Ba and Sr being considerably less. Lithium possesses a buffering action, reducing the influence of the other elements. The relative error in determining K is $\pm$ 1%. C. D. KOPKIN

3852. **Aqueous solution of potassium permanganate as a filter for the determination of potassium with a flame photometer.** K. Jaroszewicz (Dept. of General Chem., Medical Acad., Białystok). *Chem. Anal., Warsaw*, 1957, **2** (1), 97–104.—A filter, made by filling an absorption cell (8 mm thick) with 1·8% $KMnO_4$ soln., compares satisfactorily with the Zeiss K 77 filter when used in conjunction with the Zeiss Model III flame photometer; it is stable for 48 hr. K. F. SPOREK

3853. **Determination of rubidium and caesium in rocks, minerals and meteorites by neutron-activation analysis.** M. J. Cabell and A. A. Smales (A.E.R.E., Harwell, England). *Analyst*, 1957, **82**, 390–406.—The sample (10 to 250 mg) in a sealed silica ampoule and standard soln. of RbCl and CsCl in similar ampoules are irradiated in the Harwell pile. The irradiated sample is transferred to a platinum crucible, known amounts of RbCl and CsCl are added, and the mixture is heated with Na_2O_2 at 470° for 1 hr. The sinter is leached with water and the soln. is boiled, then cooled and treated with $FeCl_3$ and HCl. The soln. is made alkaline, centrifuged and filtered, and the filtrate is acidified with glacial acetic acid, heated with $FeCl_3$ and filtered. The alkali metals are then pptd. as the cobaltinitrites. The collected ppt. is dissolved in dil. HNO_3, the soln. is evaporated to dryness, the residue is dissolved in water, and the Rb and Cs are separated by means of an ion-exchange column and are then pptd. as cobaltinitrites, which are finally converted into the chloroplatinates. In this form the ppt. are weighed and counted for beta - gamma activity, the standards also being counted under identical conditions. Finally the radiochemical purity of the products is confirmed. A. O. JONES

3854. **Spectrochemical determination of caesium in igneous rocks, using a chemical concentration procedure.** C. J. Liebenberg (Univ. of Pretoria, S. Africa). *Geochim. et Cosmoch. Acta*, 1956, **10** (3), 196.—The sample (1 g, −120 mesh) is heated in a platinum basin with H_2O (5 ml), HF (20 ml) and H_2SO_4 (1 + 1) (1 ml). The soln. is evaporated to dryness; the residue is gently ignited, cooled and taken up in warm H_2O containing 0·5 g of ammonium carbonate and 4 drops of conc. aq. NH_3. After 30 min. the soln. is filtered (without washing) and the filtrate is evaporated to dryness; the residue is ignited to remove ammonium salts and the concentrate is collected, ground finely and the electrodes are filled. The Cs is determined by the spectrographic procedure of Ahrens, by either the total internal energy method or with Na as a variable internal standard. The min. limit of detection is 0·1 p.p.m. of Cs in the concentrate; $\simeq$ 6 samples can be analysed in a day. W. J. BAKER

3855. **Determination of copper in copper-plating solutions with ethylenediaminetetra-acetic acid.** F. W. Gutman. *Plating*, 1956, **43**, 345–346.—Copper is determined by titrating a sulphate soln., brought to $\simeq$ pH 6 with aq. NH_3, with EDTA (disodium salt), with murexide indicator. The colour change is brown through green to reddish purple. Cyanide soln. must be oxidised with H_2O_2 and boiled to fuming with H_2SO_4. Results are 0·2 to 0·6% higher than those obtained with thiosulphate, but the method is simpler, faster and more accurate. CHEM. ABSTR.

3856. **Colorimetric determination of traces of copper in graphite with sodium diethyldithiocarbamate.** K. Gorczyńska, D. Ciecierska and H. Walędziak (Dept. of Tech. Physics, Inst. General Chem., Warsaw). *Chem. Anal., Warsaw*, 1957, **2** (1), 52–61.—The sample (4 to 30 g) is ashed in a stream of oxygen in a platinum boat which is heated in a quartz furnace at 800° to 900°. The ash is dissolved in a mixture of HF, $HClO_4$ and H_2SO_4. Gum arabic soln. (1%) (2 ml), 20% ammonium citrate soln. (2 ml), 2·5% EDTA (disodium salt) soln. (1 ml) and aq. NH_3 to give a pH of 9 are added to the soln., and the excess of EDTA is complexed with 0·1% $MgSO_4$ soln. (1 ml); 0·1% Na diethyldithiocarbamate soln. in ethanol - water (1:4) (2·5 ml) is added and, after dilution, the extinction at 470 mμ is measured. The method will determine a few p.p.m. of Cu and it gives satisfactory results with reactor graphites containing also Fe, Co, Ni, Sb and Cd. K. F. SPOREK

3857. **Controlled potential electrolysis. IX. Electrolytic separation of copper from bismuth by the use of EDTA.** Hisao Hayakawa, Masayoshi Ishibashi and Taitiro Fujinaga. *Bull. Inst. Chem. Res., Kyoto Univ.*, 1956, **34** (6), 295–306 (in English). —This paper has been published, in Japanese, in *Japan Analyst*, 1955, **4** (10), 610. (*Cf. Anal. Abstr.*, 1956, **3**, 2416.) F. J. M.

3858. **Di(allyldithiocarbamyl)hydrazine as an analytical reagent: determination of silver and its separation from zinc.** N. K. Dutt and K. P. Sen Sarma (Dept. Inorg. Chem., Univ. Coll. Sci., Calcutta). *Sci. & Cult.*, 1956, **22** (6), 344.—Silver is quant. pptd. in the cold from a citric acid medium at pH 4·7 to 5·1 by an ethanolic soln. of the reagent. If Zn is present it may be pptd. from the filtrate after raising the pH by Na acetate and NaOH. The silver compound is washed with water and methanol, dried at 75° and weighed as $AgC_8H_{13}N_4S_2$. N. E.

3859. **New methods of analysis of silver solder.** Z. S. Mukhina. Report of symposium: Sovrem. Metodȳ Anal. Metall., M., Metallurgizdat, 1955, 194–197; *Ref. Zhur., Khim.*, 1956, Abstr. No. 22,762.—Dissolve the solder (0·5 g) in 15 ml of HNO_3, boil out oxides of N, add 0·1 *N* HCl to precipitate AgCl completely and, after 30 to 60 min., filter off the ppt. and wash it with hot water. Collect the filtrate in a 500-ml flask and make up to volume. Add conc. HCl (10 ml) and conc. H_2SO_4 (1 ml) to 20 ml of the soln. and evaporate to dryness. Dissolve the residue in 50% HCl (5 ml), add 10 ml of water and transfer to a 100-ml flask. Add aq. NH_3 till alkaline and make up to the mark. Obtain a polarogram for Cu at − 0·56 V, Cd at − 0·8 V and Zn at − 1·4 V. The basal soln. consists of 100 g of NH_4Cl, 100 ml of aq. NH_3, 50 g of Na_2SO_3 and 100 ml of 1% dextrin soln. made up to 1 litre. Zinc may be determined by amperometric titration with Na diethyldithiocarbamate soln. with a mercury cathode after removal of Cu, Cd and Ni with alkali. Silver is determined by titration with diethyldithiocarbamate after dissolving the AgCl in alkali and acidifying to dimethyl yellow. Cadmium may also be determined (after removal of Ag as AgCl and Cu with $Na_2S_2O_3$) by titration with 5:6-benzoquinoline after the addition of KI soln. C. D. KOPKIN

3860. **Estimation of gold as the element.** S. Cosma and I. Lupşa (Lab. Central Chim. al Trustului Minier, Gurabarza, Brad, Romania). *Stud. Cercet. Chim., Cluj*, 1956, **7** (1–4), 95–99.—Hexamine is used as the source of formaldehyde to reduce ionic gold in HNO_3 soln. to elementary gold by boiling with NaOH. H. SHER

3861. **Gold and palladium: their diethyldithiocarbamate complexes. Composition, structure and analysis.** M. Bobtelsky and J. Eisenstadter (The Hebrew Univ., Jerusalem, Israel). *Anal. Chim. Acta*, 1957, **16** (5), 479–487.—Gold and Pd^{2+} are titrated successively in the same soln. with standard soln. of Na diethyldithiocarbamate (0·00135 to 0·0066 *M*) by the heterometric method (*cf. Anal. Abstr.*, 1956, **3**, 12). The composition of the palladium complex and three gold complexes is deduced from the titration curves. W. C. JOHNSON

3862. **Spectrophotometric determination of beryllium with Eriochrome cyanine R.** Shunji Umemoto (Okayama Univ., Misasa Hot Springs, Tottori Prefecture). *Bull. Chem. Soc. Japan*, 1956, **29** (8), 845–852.—Eriochrome cyanine R (**I**) in tartrate soln. at pH 9·2 gives a pinkish-red colour with Be which may be used for the determination of microgram quantities of Be. Interference is caused by Zr, Fe, Al, Mg, Ti, Ca, U, Th, SiO_3^{2-}, F^- and PO_4^{3-}. *Procedure*—Dissolve K Na tartrate (0·5 g) and borax (0·191 g) in the sample (20 ml, containing 1 to 10 μg of Be), dilute to 25 ml and keep at 15° for 1 hr. Add 0·5% soln. of **I** (1 ml) and measure the extinction at 527 mμ after 4 hr. Calculate by reference to a calibration curve. A. R. ROGERS

3863. **A rapid method for fluorimetric determination of beryllium.** J. M. Riley (U.S. Bureau of Mines, Rapid City, S. Dakota, U.S.A.). *U.S. Bur. Mines, Rep. Invest.*, 1956, No. 5282, 9 pp.—The method gave reliable results on samples in the range 0·01 to 0·37% of BeO, and is particularly applicable to low-grade BeO ores. Semi-quant. determinations have been made on beryl containing 12% of BeO. Pulverise the sample to pass through a 200-mesh screen, mix well, and digest 20 mg of high-grade ore or 500 mg of low-grade rock in a platinum dish with 1 ml of conc. H_2SO_4, 1 ml of HNO_3 and 10 ml of 50% HF. Evaporate to dryness on a hot-plate, and ignite over a burner until SO_3 is expelled to remove all free acid. Fuse the residue with 5 g of fusion mixture (Na_2CO_3 - anhyd. $Na_2B_4O_7$, 3:1) for 5 min. at 1000° in a muffle-furnace. Digest the fusion cake with 25 ml of H_2SO_4 (1:1) and filter into a 1-litre flask. Transfer several equal portions containing up to 10 μg of BeO from the unknown soln. into 100-ml beakers. This is a trial-and-error method operation which must be arrived at by familiarisation with the work. Adjust the pH to 2 with 2 *M* NaOH and add 10 ml of chelating soln. (86 g of H_3BO_3, 154 g of citric acid, 288 g of NaOH and 150 ml of Versene T, diluted to 3 litres with water). Adjust the vol. to approx. 20 ml with water, mix, and bring to boiling-point on a hot-plate. Cool the soln., add 10 ml of morin soln. (0·01% in reagent-grade methanol), transfer to a 100-ml flask, add water to make the vol. 100 ml and mix well. The pH of this final soln. is approx. 13·1. Measure the percentage transmission in a fluorimeter. Prepare standard soln. of Be in the same manner as the unknowns, and prepare a standard curve ranging in BeO content from a blank to 10 μg. These

curves should be prepared daily and checked at frequent intervals while running a series of unknowns. Determine the Be in the unknown soln. from the standard calibration curve.

CHEM. ABSTR.

3864. **Separation of beryllium from iron, aluminium and titanium by ion exchange, and its application to the analysis of beryl.** M. N. Nadkarni, M. S. Varde and V. T. Athavale (Atomic Energy Estab., Bombay, India). *Anal. Chim. Acta*, 1957, **16** (5), 421–425.—The sample of beryl (0·5 g) is brought into soln. by fusing with NaF, heating the resulting cake with dil. H_2SO_4 (1:1) to fuming and dissolving the residue in 150 to 200 ml of water. The soln. is treated with 20 ml of 10% EDTA (disodium salt) soln., diluted to 400 ml and the pH adjusted to 3·5 with 10% NaOH soln. If Ti is present, 1 ml of H_2O_2 soln. (100 vol.) is added. The soln. is then passed at a rate of 5 to 6 ml per min. through a column (12 cm long × 1·8 cm diameter) of Amberlite IR-120 cation-exchange resin (Na form). The EDTA complexes of Al and Fe pass through the column, together with Ti in the oxidised anionic form, while Be is retained. The column is washed with 150 ml of 0·5% EDTA soln. of pH 3·5 and then with 100 ml of water, or with 200 ml of water if PO_4^{3-} are present. The Be^{2+} are eluted with 150 ml of 3*N* HCl followed by 100 ml of water, and determined by pptn. with aq. NH_3 and ignition to BeO. W. C. JOHNSON

3865. **Apparatus for optical determination of the end-point in the titration of calcium and magnesium with ethylenediaminetetra-acetate (EDTA).** M. Wallraf (Forschungsinst. der Zementind., Düsseldorf). *Z. anal. Chem.*, 1957, **156** (5), 332–335.—An optical system is described comprising a 6-V, 50-W bulb at the focus of a lens (f = 75 mm), an interference filter (max. transmission 620 mμ) and a selenium cell. Accommodation is provided between the filter and the cell for a 600-ml beaker standing on a magnetic stirrer. The whole is enclosed in a metal housing from which the cell must be insulated to avoid pick-up of currents induced by the stirrer. The bulb is supplied by a secondary battery to avoid fluctuations in intensity. A galvanometer is required with sensitivity of 4×10^{-9} amp. per mm. The apparatus is easily constructed and, with either murexide or Eriochrome black T indicator, will detect 1 drop of 0·001 *M* EDTA, giving a precision at least as good as gravimetric methods.

G. BURGER

3866. **Ethylenediaminetetra-acetate separation of calcium from uranium for flame-photometric analysis.** J. H. Stewart, jun., and R. C. McIlhenny (Union Carbide Nuclear Co., Oak Ridge, Tenn., U.S.A.). *U.S. Atomic Energy Comm.*, Rep. Y–1140, 1956, 14 pp.—A method is described for the determination of Ca in a uranium matrix by a rapid and relatively sharp separation of the Ca from the U, followed by a flame-photometric determination of the Ca concn. The separation is effected by using the strong complex formed between Ca^{2+} and EDTA (disodium salt) in a basic soln. A corresponding complex between UO_2^{2+} and EDTA does not form in a basic soln. The accuracy and precision are greater than those obtained by spectrographic analysis, and the method is more rapid than $KMnO_4$ titration. NUCLEAR SCI. ABSTR.

3867. **Comparisons of national radium standards.** T. P. Loftus, W. B. Mann, L. F. Paolella, L. L. Stockmann and W. J. Youden (Nat. Bur. of Standards, Washington, D.C., U.S.A.). *J. Res. Nat. Bur. Stand.*, 1957, **58** (4), 169–174.—The national primary Ra standards of Germany, Canada (new standard, 1955) and the U.S.A. (two standards) have been compared by measurements with the standard electroscope and the radiation balance. The results, and a re-assessment of those previously made on the U.S.A. and British standards (*Ibid.*, 1954, **53**, 267, 273), agree with Hönigschmid's values to within 0·2%. All six standards compared are Hönigschmid standards. W. J. BAKER

3868. **Rapid routine method for the determination of zinc in wood preservatives.** W. J. Wilson (Forest Res. Inst., Whakarewarewa, Rotorua, New Zealand). *Anal. Chim. Acta*, 1957, **16** (5), 419–420.—The method previously described (*Anal. Abstr.*, 1957, **4**, 1140) is improved by adding glycine to the soln., adjusting to pH 7·0 ± 0·5 and pptg. the Zn as phosphate. Copper and CrO_4^{2-} remain in soln. The ppt. is filtered off, dissolved in dil. H_2SO_4 and titrated with standard $K_4Fe(CN)_6$, *o*-dianisidine being used as indicator.

W. C. JOHNSON

3869. **Amperometric titration of zinc, cobalt and copper with potassium tetrathiocyanatomercuriate.** V. A. Khadeev and A. I. Mirbadaleva (V. I. Lenin Central Asia State Univ., Tashkent). *Zhur. Anal. Khim.*, 1956, **11** (6), 710–713.—Titrations with $[Hg(SCN)_4]^{2-}$ are carried out at an applied voltage of 0·7 V with the dropping mercury electrode or a rotating platinum electrode. With neutral and acid soln. of Zn and Co, satisfactory results are obtained, but the amperometric determination of Cu is impossible because of variability in the composition of the ppt. obtained. G. S. SMITH

3870. **Di(allyldithiocarbamyl)hydrazine as an analytical reagent. Determination of mercury and its separation from lead.** N. K. Dutt and K. P. Sen Sarma (Univ. Coll. Sci., Calcutta). *Sci. & Cult.*, 1956, **22**, 239–240.—The sodium salt (**I**) of di(allyldithiocarbamyl)hydrazine was prepared by neutralisation with Na_2CO_3. Mercury was pptd. from a soln. of mercury and lead nitrates by **I** at a pH of 3 to 3·5. The ppt. was allowed to settle for 1 hr., then collected in a Gooch crucible, washed with H_2O, abs. ethanol, and dry ether, dried, and weighed as $Hg(C_8H_{12}N_4S_2)$. CHEM. ABSTR.

3871. **Iodimetric determination of mercury and silver.** J. Foucry. *Peint. Pigm.-Vern.*, 1957, **33** (1), 52.—The mercury or silver salt or complex of the compound to be determined is pptd. by the appropriate reagent, *e.g.* Nessler, Denigès, or mercuric thiocyanate, the ppt. is centrifuged and washed, then dissolved in HNO_3 and boiled to destroy oxidisable matter. A 10-ml aliquot of the soln. is titrated with a soln. of iodine in KI, with starch as indicator, until the blue colour just persists. All soln. are diluted to 0·002 *N* at the moment of titration. F. J. M.

3872. **Micro-determination of heavy elements such as mercury and iodine, in solution, by X-ray absorption.** J. Leroux, P. A. Maffett and J. L. Monkman (Dept. of National Health and Welfare, Ottawa, Canada). *Anal. Chem.*, 1957, **29** (7), 1089–1092.—By carefully selecting the absorption cell and radiation, a fraction of a microgram can be

determined in a vol. of less than 1 μl. The sensitivity of the method for a particular element or compound can be predicted from a simple empirical equation. Absorption cells with a vol. of 0·5 μl are made from capillary tubing of 0·16 mm internal diameter. K. A. PROCTOR

3873. **The use of NNN′N′-tetrakis(2-hydroxypropyl)ethylenediamine in the determination of the R_2O_3 group in limestone.** V. H. Dodson and A. H. Black (Univ. Toledo, Toledo, Ohio, U.S.A.). *Ohio J. Sci.*, 1956, **56**, 147–150.—A quant. pptn. of Fe^{3+} and Al^{3+} occurs in the presence of NNN′N′-tetrakis(2-hydroxypropyl)ethylenediamine (**I**) over a pH range of 6·0 to 6·5, with negligible co-pptn. of Ca^{2+} and Mg^{2+}. A comparison of the analyses of R_2O_3 content of 8 samples of limestone and dolomite, having from $< 0·5$ to $> 5\%$ of Fe_2O_3 and Al_2O_3 content, by using the standard double-pptn. method with aq. NH_3 and a single pptn. with **I**, showed excellent agreement between the two methods. CHEM. ABSTR.

3874. **Determination of traces of boron in silicon.** G. H. Morrison and R. L. Rupp (Chem. Lab., Sylvania Electric Products, Inc., Flushing, N.Y., U.S.A.). *Anal. Chem.*, 1957, **29** (6), 892–895.—The silicon, containing 0·001 to 1 p.p.m. of B, is dissolved in dil. NaOH and the soln. is electrolysed between platinum electrodes in a polyethylene cell (described). After approx. 5 hr., the anolyte, which is separated from the bulk of the soln. by a cation-permeable membrane, is evaporated to dryness and the residue is extracted with water and the extracts are evaporated to dryness. The final residue is subjected to spectrographic analysis under argon, with In as an internal standard. The concn. of B is evaluated by comparison of the lines at 2497·7 A obtained with a log-step sector in the sample and in standards. Precision data are given, and it is stated that blanks are very low, and that the procedure could be extended to other impurities in silicon. D. A. PANTONY

3875. **The separation of trace amounts of boric acid from silicic acid by perforation.** F. A. Pohl (AEG-Forschungsinst., Belecke, Germany). *Z. anal. Chem.*, 1957, **157** (1), 6–13.—Methods for the separation of H_3BO_3 from H_2SiO_3 by distillation and extraction are discussed critically. The solubility of H_3BO_3 in several alcohols and ethers, and the corresponding extraction coeff., are listed. Conditions for the extraction of H_3BO_3 with methanol - *iso*propyl ether have been established and a suitable "perforator" (extractor with sintered-glass solvent distributor) is described. The procedure is simple, rapid and trouble-free. Compared with the ester method, the perforation procedure is much more sensitive, besides facilitating the complete separation of microgram amounts of B from gram amounts of H_2SiO_3. W. J. BAKER

3876. **The direct titration of boric acid in nickel and other electrolytes with a fluorescent indicator.** L. A. Maĭ. Report of symposium: Sovrem. Metodȳ Anal. Metall. M., Metallurgizdat, 1955, 211–213; *Ref. Zhur., Khim.*, 1956, Abstr. No. 22,739.—Dilute the electrolyte (20 to 25 ml), containing up to 150 mg of H_3BO_3, and up to 0·5 *N* in Ni, Co, Cd and Mn, five times, just acidify with H_2SO_4, boil for 3 min. to remove CO_2, cool, add six drops of indicator (0·06% methyl red and 0·06% fluorescein in ethanol), and adjust the pH to between 5·8 and 6·2. Then add 50 ml of a soln. of invert sugar, cool in ice, and titrate the red soln. with 0·1 *N* alkali to a green fluorescence. The titration is complete when the addition of invert sugar does not alter the intensity of the fluorescence. The average error is $< 1\%$. The free H_3BO_3 may be titrated in the presence of fluoroborates and fluorosilicates. Large quantities of Mg and Zn, and SCN^-, Al and Cr interfere, but not other probable constituents of electroplating soln. C. D. KOPKIN

3877. **Rapid determination of aluminium in alloys containing iron or nickel.** M. F. Klimovskaya. Report of symposium: Sovrem. Metodȳ Anal. Metall., M., Metallurgizdat, 1955, 185–187; *Ref. Zhur., Khim.*, 1956, Abstr. No. 22,701.—Dissolve the alloy (1 g) in 50 ml of HNO_3 (1:1), evaporate to about 20 ml, dilute and add 10% NaOH soln. to precipitate $Fe(OH)_3$, $Ni(OH)_2$ and $Cu(OH)_2$, and 50 ml in excess, heat to boiling, cool and dilute the soln. and ppt. to 500 ml. Filter and neutralise 50 ml of the filtrate with HCl (1:1) to phenolphthalein and add a few drops more of HCl until the soln. is clear. Heat to boiling, neutralise with 0·1 *N* NaOH to a clear red colour and add 25 ml of 0·2 *N* HCl, $\simeq$ 5 ml of *N* K oxalate soln. and 5 g of NaCl. Boil to dissolve the ppt. (10 to 15 min.), cool, add about 5 ml of neutral 2 *N* $MgCl_2$, and titrate very slowly and with vigorous stirring with 0·1 *N* NaOH to methyl red. The quantity of Al_2O_3 equivalent to 1 ml of 0·1 *N* HCl is best established empirically with metallic aluminium. The determination takes 3 hr. C. D. KOPKIN

3878. **Determination of aluminium in aluminium - iron alloys.** J. V. Gilfrich (U.S. Naval Ordnance Lab., Silver Spring, Md., U.S.A.). *Anal. Chem.*, 1957, **29** (6), 978–980.—The sample is dissolved in aqua regia, the soln. is evaporated to dryness and the residue taken up in HCl. The soln. is run through a cation-exchange column (Dowex-1), which does not retain Al in 8 *N* HCl. The eluate, containing the Al, is treated with HNO_3 to destroy organic matter, and evaporated to dryness, and the residue is taken up in HCl. The Al is pptd. with aq. NH_3 and ignited to Al_2O_3 by standard methods. A standard deviation of $\pm$ 0·03% on a sample containing 14% of Al is quoted. D. A. PANTONY

3879. **Direct spectrochemical determination of aluminium in lime-soda glasses by photometric methods.** F. Hegemann and V. Caimann (Tech. Hochschule, Munich). *Glastech. Ber.*, 1956, **29**, 239–247.—For an accurate and rapid direct determination of Al in glass a method was developed which was based on the use of the photo-electric spectrophotometer of Scheibe, modified by Krempl *et al.* (*cf. Z. angew. Phys.*, 1956, **8**, 16). For the emission spectral analysis the sample powder is mixed with purest spectral carbon powder and compacted under a hydraulic pressure of 2500 kg per sq. cm to rod electrodes. The emission is made in a condensed spark. The details of the method, and the corrections for unavoidable errors are extensively discussed. Typical checking curves, and intensity *vs.* time curves for Al, Ga, Si, C and Sn as test materials as well as curves for the scattered background light are given, with a comparison for the results of the chemical and the spectral-analytical determinations of Al (as Al_2O_3) in glass samples from different batches. The reproducibility and accuracy are highly satisfactory (errors of $\pm$ 1·7% for the integral reproducibility, $\pm$ 0·4% for concn. of 0·8% of Al_2O_3 in the glass, and $\pm$ 1·06% for 0·3% of Al_2O_3). CHEM. ABSTR.

3880. **Spectrographic determination of alumina in lead borosilicate glass frits.** A. M. Liebman (Pittsburgh Plate Glass Co., Creighton, Pa., U.S.A.). *Anal. Chem.*, 1957, **29** (6), 899–902.—In the method, which covers the range 1·30 to 8·00% of alumina, the finely ground sample is mixed with graphite powder, containing cobaltic oxide as internal standard, and excited in a d.c. arc. A systematic study of matrix effects showed that the method gave excellent results over relatively wide matrix changes. The precision, expressed as coefficient of variation, is ± 2·3% of the amount present, for triplicate determinations. K. A. PROCTOR

3881. **Determination of gallium by spectrophotometry in the presence of aluminon.** E. Rinck and P. Feschotte (Lab. de Chim. Appl., Fac. de Sci., Paris, France). *Bull. Soc. Chim. France*, 1957, (2), 230–234.—Quantities of Ga of the order of 1 to 50 μg may be determined with an accuracy of ± 1 μg. *Procedure*—The soln. containing Ga (< 50 μg) is neutralised with *N* NaOH. Bromophenol blue soln. (0·1%) is added and the pH is adjusted to 3·8. The operation is now repeated with a second portion without the indicator, and the soln. is made up to 50 ml with water. To this soln. (20 ml) are added 2 *M* acetate buffer (pH = 3·8) (20 ml) and aluminon (0·1% aq. soln.) (50 ml). After 20 min. the colour is estimated spectrophotometrically at 525 mμ and compared with a blank soln. of reagents. The Ga is found by comparison with a standard curve. C. A. SLATER

3882. **New microchemical reaction of thallium.** Carmelo Fazio C. *Rev. Asoc. Bioquim. Argentina*, 1956, **21**, 194–203.—Microchemical reactions of Tl are briefly reviewed and a new reaction for the microcrystalloscopic detection of Tl^+ is proposed. *Procedure*—Evaporate a drop of the neutral test soln. to dryness at low temp. on a microscope slide, and treat the residue with a drop of *N* $Na_2S_2O_3$, followed by a drop of ethanol (95%). If Tl^+ are present, characteristic crystals in the form of needles and stars, readily seen under the microscope, will be formed. There is no interference from Ag^+, Pb^{2+} and Hg^+. The limit of detection is 1 in $2·5 \times 10^4$. G. H. FOXLEY

3883. **New photometric method for determining thallium with rhodamine B.** Hiroshi Onishi (Gov. Ind. Res. Inst., Nagoya). *Bull. Chem. Soc. Japan*, 1956, **29** (8), 945.—Oxidation of Tl^I to Tl^{III} with Br is a satisfactory method preparatory to colorimetric micro-determination of Tl with rhodamine B. *Procedure*—Heat the sample (containing 2 to 10 μg of Tl) with 2 *N* HCl (5 ml) and saturated bromine water (0·5 ml) until the colour of Br has disappeared, cool and dilute to 10 ml with 2 *N* HCl. Mix with 0·2% rhodamine B soln. (1 ml), extract with benzene (10 ml), allow to separate and measure the extinction of the benzene extract at 560 mμ. The molar extinction coeff. is ≃ 87,000.
A. R. ROGERS

3884. **Spectroscopic method for the estimation of thallium.** D. Peschanski (Lab. de Chim., Fac. des Sciences, Paris). *Bull. Soc. Chim. France*, 1956, (11–12), 1574.—Microgram quant. of Tl are estimated spectrophotometrically in the u.v. as the complex $[TlCl_6]^{3-}$, which is formed in 6 *M* HCl. The complex shows high extinction values between 225 and 300 mμ, with a max. between 240 and 260 mμ. Other ions, especially cations, must be absent. Univalent Tl must be oxidised with Cl; NO_3^- interfere if present in concn. in excess of that of the Tl. J. H. WATON

3885. **New photometric determination of thallium in lead, zinc and cadmium.** H. Pohl (Bundesanst. für Materialprüfung, Berlin-Dahlem). *Erzmetall*, 1956, **9** (11), 530–531.—Trace amounts of Tl are quant. separated by extraction from bromide soln. with *iso*propyl ether, followed by conversion into the Tl - diethyldithiocarbamate complex in the same solvent. The extinctions of this *iso*propyl ether soln. and of a blank are measured against that of the pure solvent at 315 mμ. The results show a relative error of ≯ 10%. J. H. WATON

3886. **Separation of the rare earths by means of ethylenediaminetetra-acetic acid.** J. Fuger (Univ. of Liège, Belgium). *Bull. Soc. Chim. Belg.*, 1957, **66** (1–2), 151–168.—An extensive study has been made of the chromatographic separation of the rare earths on Dowex 50 by elution with EDTA. Small changes in pH have a considerable influence on the separation, but if the pH is accurately controlled a good separation of mixtures of Y, Eu, Pm, Nd, Pr and Ce can be obtained. Other rare-earth mixtures (Lu, Tm, Ho, Y, Tb, Gd, Eu) may be separated on columns of Dowex 50 (metal form), the corresponding metal complex of EDTA being used for elution. Tests with Zn, Ca and Co have shown the best separations to be obtained with Zn. From the results the stability constant of Pm with EDTA has been calculated as $10^{-16·75}$.
C. A. SLATER

3887. **Determination of actinium in minerals.** M. Perey and A. Hettler. *Compt. Rend.*, 1956, **243** (20), 1520–1522.—The actinium in any radioactive mineral can be extracted directly as AcX by separation as sulphate in the presence of Ba as carrier, followed by conversion into carbonate and then into chloride. The final soln. (≃ 0·5 *N* HCl) is boiled for 10 min. and Ra, Th and AcX are removed by co-pptn. on PbS, a second pptn. being made ≃ 30 min. later to isolate the AcX, which alone has by then attained equilibrium. The activity of the deposit is then measured by the procedure described previously (*Compt. Rend.*, 1956, **242**, 2552). The sensitivity is claimed to exceed that of all the other methods, *e.g.*, 0·01 μC of Ac can be determined in the presence of 1 μC of Ra to within ≃ ± 5%. The procedure, which is specially useful for radioactive minerals insol. in acids, is also valid in the presence of La.
W. J. BAKER

3888. **Fluorimetric method for estimation of cyanide. Application to estimation of free hydrogen cyanide in ethyl dimethylphosphoramidocyanidate vapour.** J. S. Hanker, R. M. Gamson and H. Klapper (Chem. Warfare Lab., Army Chem. Center, Md., U.S.A.). *Anal. Chem.*, 1957, **29** (6), 879–881.—After separation of the phosphoroamidocyanidate (tabun) in diethyl phthalate, HCN in the air samples is absorbed in aq. KOH. This soln. is made up to standard vol. with aq. soln. of $KHCO_3$, nicotinamide and chloramine T and water, and, after 3 min., more KOH. The max. increase in fluorescence is measured and compared with that of a standard CN^- soln. Variables in the determination are examined and the method is checked by a determination of total CN^-. The fluorescence approximately follows the Beer - Bouguer law.
D. A. PANTONY

3889. **Photometric determination of small amounts of silicon in nickel and nickel alloys used in electronic devices.** T. R. Andrew (Mullard Radio Valve Co. Ltd., Mitcham Junction, Surrey, England). *Analyst*, 1957, **82**, 423–427.—The procedure described is suitable for the determination of Si in nickel and nickel alloys containing up to 4% of W. The sample is dissolved in HNO_3 (with H_3PO_4 if W is present). An aliquot of the diluted soln. is treated with ammonium molybdate soln., the temp. is brought to 25° ± 2° and the mixture is set aside for 20 min. Oxalic acid soln. and a reducing soln. (ferrous and ferric ammonium sulphates in dil. H_2SO_4) are then added. An equal aliquot is treated with the same amounts of the reagents, but the ammonium molybdate soln. is added after the other two. The extinctions of the two liquids are measured at 810 mμ against water. A precision of ± 0·001% of Si is claimed with a sample weighing 0·25 g, and the method can be applied to samples weighing only 12·5 mg, such as may be available as single cathodes from electronic valves.

A. O. JONES

3890. **Quantitative spectral analysis of silicon carbide with spark excitation.** F. Hegemann, K. Giesen and C. von Sybel. *Ber. dtsch. keram. Ges.*, 1956, **33** (12), 387–390.—The Q.24 Zeiss spectrograph was used with a condensed d.c. arc, a sample/C pastille (1/1·5) and Ni as the external standard. The lines used were Ni 3050·8, Ti 3088·0, Fe 2599·6 and Al 3092·7 A. Measurements on a standard sample of SiC from the Nat. Bur. Standards and a pure sample (Philips, Eindhoven) gave results within ± 2·2, 1·9 and 3·2% of the true value for Fe, Al and Ti, respectively.

J. A. SUGDEN

3891. **Photometric determination of germanium as molybdovanadogermanic acid.** Z. F. Shakhova and R. K. Motorkina (M. V. Lomonosov Moscow State Univ.). *Zhur. Anal. Khim.*, 1956, **11** (6), 698–703.—Two methods are described. In the first, 0·01 to 1 mg of GeO_2 is treated with 0·5 ml of 5% ammonium molybdate soln. and 0·05 to 0·12 ml of 2 *N* H_2SO_4 (to give an acid concn. of 0·2 *N*) and then, after complete development of the yellow colour (10 min.), with 5 ml of 2% $NaVO_3$ soln., previously neutralised to methyl orange paper with 2 *N* H_2SO_4, and 0·8 ml of 2 *N* H_2SO_4. The soln. is boiled for 1 to 2 min., kept at 100° for 30 min., and filtered from the brown ppt., which is washed with 10% NH_4Cl soln., and the extinction measured at 400 mμ. The second method is based on the use of a previously mixed reagent. Better results are obtained by extracting the complex in *iso*amyl alcohol.

G. S. SMITH

3892. **Quantitative analyses by fluorescent X-ray spectrography. Determination of germanium in coal and coal ash.** W. J. Campbell, H. F. Carl and C. E. White (Bureau of Mines, College Park, Md., U.S.A.). *Anal. Chem.*, 1957, **29** (7), 1009–1017.—Four general methods for correlating line intensity or line-intensity ratios to concn. have been developed. (*i*) Direct comparison with standard samples can be used to survey 50 to 100 samples per day; (*ii*) internal standardisation is accurate to within ± 10% of the amount present for concn. of Ge exceeding 0·1%, with decreasing accuracy for lower values; (*iii*) addition techniques with the same accuracy as method (*ii*); (*iv*) preliminary chemical separation with subsequent excitation of the concentrated fraction of Ge is believed to be accurate to within ± 10% for concn. > 0·001%. The lower limit of detection by methods (*i*), (*ii*) and (*iii*) is approx. 0·01%, and, by method (*iv*), 0·0002 to 0·0004%. Studies in the loss of Ge on thermal ashing show that no detectable amounts are lost below 600°.

K. A. PROCTOR

3893. **Colorimetric determination of germanium in coal by a wet-decomposition method. I. Conditions of analysis.** Mitsuru Ura (Ind. Res. Inst. of Kanagawa Prefecture, Kanazawa-ku, Yokohama). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1957, **78** (3), 316–320.—Coal (≃ 1 g) is readily decomposed with $K_2Cr_2O_7$ (20 g) in a mixture of H_2SO_4 (≃ 30 ml) and conc. H_3PO_4 (≃ 20 ml) (*cf.* Kiba *et al.*, *Anal. Abstr.*, 1955, **2**, 2371) by gradual heating to 140° to 160°; any Ge present passes into solution. The excess of $K_2Cr_2O_7$ is decomposed with aq. $NaHSO_3$ soln. (≃ 2·5 g in 70 ml of water) and the product is mixed with conc. HCl (30 ml) and distilled. The distillate (30 ml) is mixed with sufficient 6 *N* HCl to give 50 ml of 1·2 *N* HCl soln., poly(vinyl alcohol) (as protective colloid, 0·25%, 5 ml) and ethanolic 0·04% phenylfluorone soln., and made up to 50 ml. The extinction of the resulting soln. is measured at 510 mμ. The presence of an excess of an oxidising or a reducing agent does not interfere with the distillation of Ge. The colorimetry is affected by the presence of oxidising agents but not by SO_2. The distillate is treated with one drop of 6% SO_2 soln. Lignites and brown coals are decomposed at a lower temp.

K. SAITO

3894. **New micro-method for rapid gravimetric determination of lead.** E. Popper, V. Junie and L. Popa (Lab. Anal. Chem., Fac. Pharm., I.M.F., Cluj, Romania). *Stud. Cercet. Chim., Cluj*, 1956, **7** (1–4), 89–94.—The ppt. formed with 5-anilino-2-mercapto-1:3:4-thiadiazole has a high mol. wt., so that accurate determinations of Pb in dil. soln. of 6 μg per ml are obtained. It is claimed that the method is simple and rapid, requiring only 45 min. The determination can be made in the presence of salts of alkali metals and alkaline earths.

H. SHER

3895. **Determination of lead in organic material.** J. C. Gage (I.C.I. Ltd., Ind. Hygiene Res. Lab., The Frythe, Welwyn, Herts., England). *Analyst*, 1957, **82**, 453.—In a previously described method (*cf. Anal. Abstr.*, 1956, **3**, 1297), Pb is extracted as the diethyldithiocarbamate complex with a mixture of sulphur-free toluene and pentanol. Some specimens of toluene, although described as "sulphur-free", may yield poor recoveries of Pb. This can be avoided by treating the solvent mixture with Br until a deep-yellow colour persists and, after 30 min., decolorising the solvent with bisulphite soln. and washing it with water. In the method described (*loc. cit.*) the citrate - bicarbonate soln. should not be extracted with the solvent until 15 min. after addition of solid Na diethyldithiocarbamate, and a similar period should be allowed between the addition of this reagent to the test soln. and extraction with the purified solvent mixture.

A. O. JONES

3896. **Di(allyldithiocarbamyl)hydrazine as an analytical reagent: separation of lead and calcium.** N. K. Dutt and K. P. Sen Sarma (Dept. Inorg. Chem., Univ. Coll. Sci., Calcutta). *Sci. & Cult.*, 1956, **22** (5), 283.—The use of this reagent for

the separation of Pb from Ca has been found practicable since Ca does not interfere when the reagent is added to a soln. of the nitrates. N. E.

3897. **Polarographic determination of copper, lead, cadmium and zinc in lead concentrates.** Gh. Burlacu, O. Bot and I. Antonescu. *Stud. Cercet. Stiint. Chim., Cluj*, 1956, **7** (1), 17–23.—The concentrate is dissolved in conc. HNO_3 and, after elimination of acid by heating on a water bath, the residue is treated with $NaNO_3$ to dissolve $PbSO_4$ and precipitate Fe. After filtration the elements can be determined directly, polarographically. The method is satisfactory in dilute (0·6 *M*) as well as in conc. (3·5 *M*) soln. of $NaNO_3$.

H. Sher

3898. **Amperometric titration of titanium.** R. P. Graham and E. VanDalen (Canadian Industries Limited, Millhaven, Ontario). *Canad. J. Chem.*, 1957, **35** (4), 418–421.—Amperometric titration of Ti^{4+} with *m*-nitrophenylarsonic acid, previously believed to be unsatisfactory, has been shown to be practicable provided that the correct conditions are achieved. The pH must be carefully controlled, and both the nature and concn. of the anions in the solution are important factors. A description of the method employed is given, with results. The method used to determine the composition of the Ti *m*-nitrophenylarsonate pptd. is also described; this compound is shown to be a monoarsonate, except when there is a considerable excess of reagent, when a diarsonate is formed.

J. F. P. H. Greene

3899. **New spectrophotometric determination of a micro amount of titanium with alizarin red S.** Hidehiro Gotô, Yachiyo Kakita and Michiko Namiki (Inst. for Iron, Steel and Other Metals, Tohoku Univ., Katabira-cho, Sendai). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1957, **78** (3), 373–376.—Titanium acts as a catalyst towards the reduction of Na alizarinsulphonate (**I**) with $SnCl_2$ to give a green product having a max. absorption at 760 mμ. The extinction is proportional to the concn. of Ti for < 35 μg per 10 ml. The rate of reduction increases with increase in HCl concn., as does the rate of decolorisation, the optimum concn. being 6 *N*. The presence of oxalate, succinate, tartrate and citrate increases the extinction coeff. The sample soln. ($\simeq$ 1 ml) is mixed with conc. HCl (4 ml), ammonium oxalate (satd. soln., 2 ml), **I** (0·2%, 0·7 ml), $SnCl_2$ (20% in 6 *N* HCl, 2 ml) and made up to 10 ml. The presence of < 200 μg of foreign ions, including those of Zr, Mo, W, V, Ge, Co, Ni, Mn, Cr and Cu, < 100 mg of Zn and Al, and < 300 mg of Fe^{2+} and Fe^{3+} does not vitiate the estimation.

K. Saito

3900. **Carbon in non-ferrous metals. V. Carbon content in titanium and titanium alloys.** J. Fischer and W. Schmidt (Inst. für Anorg. Chem., J. W. Goethe Univ., Frankfurt a. Main). *Erzmetall*, 1956, **9** (9), 434–439.—A rapid and reliable method is given for the determination of small amounts of carbon in titanium and titanium alloys. Copper and a Pb - Sn alloy are added to the sample to allow a smooth and complete combustion. *Procedure*—The sample (0·1 to 1·0 g according to the carbon content) is first cleaned by treatment with a mixture of HNO_3 (sp. gr. 1·4) and 40% HF (4:1), washed with water and dried at 110°. A twofold excess of copper wire (1·5 mm) cut into $\simeq$ 1-cm lengths is laid in the combustion boat, together with $\simeq$ 10% of Pb - Sn alloy. The sample is then added, and is ignited at 1150° in a stream of moist O. The determination is completed by potentiometric titration (*cf. Anal. Abstr.*, 1956, **3**, 3583). The results show a relative error of $\gtrsim \pm$ 1·5%. Errors of $\simeq$ 15% are found in Ti - C alloys, owing to the non-homogeneity of the carbon content.

J. H. Waton

3901. **Volumetric determination of titanium and iron. I. Differential titration of titanium and iron in solution.** Shigeo Kobayashi and Ichiro Ogasawara (Gov. Chem. Ind. Res. Inst., Yoyogi P.O., Tokyo). *Rep. Gov. Chem. Ind. Res. Inst., Tokyo*, 1957, **52** (1), 21–24.—Titanium and Fe are reduced (20°, 15 min.) to the ter- and bi-valent states, respectively, with 2% zinc amalgam, and Ti is titrated with 0·1 *N* $KMnO_4$ by the use of Na_2WO_4 (1%) as indicator. Tungstate is reduced to tungsten blue with Ti^{3+} but not with Fe^{2+}. No appreciable pptn. of WO_3 is observed in 2 to 4 *N* H_2SO_4 during the course of titration. The addition of $KMnO_4$ is continued until a pink colour appears in the soln., giving the vol. required to oxidise Fe^{2+} to Fe^{3+}.

K. Saito

3902. **Spectrographic analysis of zirconium and hafnium.** D. A. Del Grosso and F. P. Landis (G.E.Co., Schenectady, N.Y., U.S.A.). *U.S. Atomic Energy Comm.*, Rep. KAPL–1539, 1956, 52 pp.—Spectrographic methods are presented for the determination of 31 metallic impurities in zirconium, zirconium alloys and hafnium. The methods described include two carrier-distillation d.c. arc methods for the determination of most of the impurities, a 2200-V a.c. arc method for W, and a high-amperage d.c. arc method for Hf:Zr ratios. As developed, the first two methods are semi-quant., *i.e.*, the results are probably accurate within $\pm$50%; the determinations of W and of Hf:Zr ratios are internal standard methods based on the intensity of a matrix line and are more precise.

Chem. Abstr.

3903. **Use of phytic acid in the analytical chemistry of thorium.** D. I. Ryabchikov, V. K. Belyaeva and A. N. Ermakov (V. I. Vernadskiĭ Inst. of Geochem. and Anal. Chem., Acad. Sci., USSR, Moscow). *Zhur. Anal. Khim.*, 1956, **11** (6), 658–667.—From neutral soln. phytic acid precipitates nearly all the cations except those of the alkali group. From *N* HNO_3 only Ti, Zr, Hf, Th, Ce^{4+}, Nb, U, Sc, In, Sn^{4+} and Fe are pptd., although from *N* HCl In and Sn^{4+} are not pptd. and from > 2 *N* HNO_3 Sn^{+4} and Fe are not pptd., whilst Ti, Zr, Hf, Th, Ce^{4+}, In and Sc are pptd. even in 12 *N* HNO_3. The quant. separation and determination of Th is studied in detail. Ignition of the ppt. at 1100° gives non-hygroscopic $Th(PO_3)_4$. In 6 *N* HNO_3, separation from the rare earths is practically quant. and Al and Ca do not interfere, but Fe tends to co-precipitate, and U, Ti and Zr are completely pptd. Interference from Ti can be prevented by addition of H_2O_2, and from U by the use of 6 *N* HCl instead of HNO_3, but pptn. free from Fe, Ti, Zr and U is possible in the presence of oxalic acid. To determine Th in monazite concentrates, the sample (10 g) is decomposed by H_2SO_4 as described by Carney *et al.* (*J. Amer. Chem. Soc.*, 1914, **36**, 1134) and the soln. (500 to 600 ml) of the sulphates is diluted to 1 litre with conc. HNO_3. An aliquot portion (100 ml) is mixed with 1 to 2 ml of 30% H_2O_2, then heated and mixed with 25 ml of 10% oxalic acid soln., followed by

5 ml of 4% phytic acid soln., and centrifuged after 15 to 20 min. The ppt. is washed by centrifuging with two 25-ml portions of washing soln. (prepared by diluting 25 ml of 4% phytic acid soln., 25 ml of 10% oxalic acid soln. and 300 ml of conc. HNO_3 to 1 litre), and then dissolved in 15 to 20 ml of diammonium hydrogen citrate. The soln. with washings (40 to 50 ml) is mixed with 30 to 40 ml of conc. HNO_3, 1 ml of 30% H_2O_2, and 4 to 5 ml of 4% phytic acid soln. to re-precipitate the Th. The ppt. is collected on paper after 15 to 20 min., washed with 4 *N* HNO_3 and ignited to const. wt. at 1100°. At concn. of 4 to 7% of Th in monazite samples the method is accurate to $\pm$ 2% of the content. G. S. SMITH

3904. **Thoron - *meso*tartaric acid system for determination of thorium.** M. H. Fletcher, F. S. Grimaldi and L. B. Jenkins (U.S. Geological Survey, Washington, D.C., U.S.A.). *Anal. Chem.*, 1957, **29** (6), 963–967.—The conditions that affect the spectrophotometric determination of Th with thoron in the presence of *meso*tartaric acid as a masking agent, especially for Zr, are investigated. The finely ground sample is sintered with excess of Na_2O_2 and the cake is dissolved in water. After decomp. of H_2O_2, and acidification, the soln. is made alkaline with a standard excess of KOH, and filtered, and the residue is dissolved in HCl and made up to a standard vol. An aliquot of this soln. is evaporated to fumes on a steam bath with $HClO_4$, which is finally removed by careful heating on a sand bath. The residue is taken up in HCl and water, and then hydroxylamine hydrochloride and a catalytic amount of Cu^{2+} are added. The soln. is digested, cooled and made up to standard vol. with aq. *meso*tartaric acid, thoron reagent and water. Absorption is measured at 545 mμ against a reagent blank and the content of Th^{4+} is calculated from a calibration curve or by the use of standards. The effects of 35 ions commonly encountered in thorium ores are tabulated.
D. A. PANTONY

3905. **Photometric determination of thorium with indo-oxine.** E. Tomic and H. Khalifa (II Chem. Inst., Univ. Wien). *Z. anal. Chem.*, 1957, **156** (5), 326–331.—Thorium can be determined in the concn. range of 0·1 p.p.m. to 6 p.p.m. Evaporate the thorium soln. to dryness and dissolve the residue in HNO_3 (2 ml). Add 2 ml of methanolic indo-oxine soln. (0·005% for samples containing < 10 μg of Th or 0·05% for > 10 μg of Th) and acetate buffer (pH 5·6) to make 10 ml. Measure the absorption at 650 mμ, against the reagent soln., within 1 hour. All cations other than alkali and alkaline-earth ions interfere; Cl^- and SO_4^{2-} do not interfere. Beer's law holds for the range 0·1 to 6 μg of Th. Temp. has no effect between 15° and 30°. Citrate, phthalate or tartrate buffers are not suitable. G. BURGER

3906. **Polarographic determinations of thorium.** R. P. Graham and G. B. Larrabee (Burke Chem. Lab., Hamilton Coll., McMaster Univ., Hamilton, Ontario, Canada). *Analyst*, 1957, **82**, 415–422.—Indirect methods are described. These involve the quant. pptn. of Th under controlled conditions by *m*-nitrophenylarsonic acid, 8-hydroxyquinoline or *m*-nitrobenzoic acid. The collected washed ppt. is dissolved in a suitable solvent so that the organic reagent is liberated, and this is then determined polarographically. The method in which Th is pptd. as the tetra-(*m*-nitrobenzoate) is shown to be applicable to the determination of Th in magnesium alloys containing Zn and rare-earth elements. The relative merits of each precipitant are discussed.
A. O. JONES

3907. **Acid requirements of the Kjeldahl digestion.** R. B. Bradstreet (Bradstreet Lab., Inc., Cranford, N.J., U.S.A.). *Anal. Chem.*, 1957, **29** (6), 944–947.—From expt. on the recovery of $(NH_4)_2SO_4$ from two types of digestion mixture it is shown that NH_3 is lost when the cold mixture approaches the solid state, and that the critical amount of acid that should be present at the beginning of a 50-min. boil is between 7·5 and 10 ml. There is loss of acid during this period (approx. 0·0355 g per min.) and during the conversion of the sample. Figures are given for 21 substances, showing acid to substance ratios from 6·27 to 19·87, and minimum digestion times from 75 to 105 min. The amount of acid required for a particular digestion can be calculated, and an "acid index" selected to give optimum conditions. It is suggested that this should not be less than 0·88 for a digest containing 10 g of K_2SO_4 and 0·68 for one containing 10 g of K_2SO_4 and 5 g of $Na_2S_2O_3.5H_2O$. The use of Na_2SO_4 to replace K_2SO_4 is regarded as unsatisfactory for refractory substances. R. E. ESSERY

3908. **Micro-determination of azides.** Yojiro Mizushima and Seietzu Nagayama (Gov. Chem. Ind. Res. Inst., Tokyo). *J. Ind. Explosives Soc., Japan*, 1956, **17**, 113–115.—For the determination by the reaction—

$$M(N_3)_2 + 2Ce(NO_3)_4.NH_4NO_3 \rightarrow 2Ce(NO_3)_3 + M(NO_3)_2 + 2NH_4NO_3 + 3\,N_2$$

mix 10 g of the sample with 3 ml of 30% aq. $Ce(NO_3)_4.NH_4NO_3$ in a CO_2 atm. and determine evolved N by a 5-ml nitrometer. The procedure takes 30 min. The error is $\pm$ 0·1% for M = Cu and Pb and $\pm$ 0·3% for Na. CHEM. ABSTR.

3909. **Determination of nitrate nitrogen by the strong phosphoric acid - iodic acid decomposition method.** Shigeru Ohashi and Hiroshi Makishima (Fac. Sci., Kanazawa Univ., Japan). *Bull. Chem. Soc. Japan*, 1956, **29** (6), 700–703.—The iodic acid decomposition method for the determination of organic nitrogen (*cf. Anal. Abstr.*, 1955, **2**, 2448; 1956, **3**, 2755) has been extended to the analysis of nitrates. The accuracy is within $\pm$ 2%. The time taken for an analysis is < 1 hr. *Procedure*—Dissolve the sample (containing 6 to 12 mg of NO_3^-) by warming with conc. H_2SO_4 (1·5 to 2 ml) containing salicylic acid (70 mg). Add $Na_2S_2O_3$ (50 mg) and heat until white fumes are evolved. Add conc. H_3PO_4 (5 ml) and cool. Add KIO_3 (1·5 g). Displace the air with CO_2. Heat to between 200° and 250° until decomposition is complete, and transfer the liberated N to a nitrometer. A. R. ROGERS

3910. **Determination of very small amounts of nitrate, nitrite and hydroxylamine.** N. S. Drozdov and A. K. Iskandaryan (Second Moscow Medicinal Inst.). *Zhur. Anal. Khim.*, 1956, **11** (6), 723–727.—Separate 10-ml portions are taken for determining NO_2^-, NO_3^- and hydroxylamine. For NO_2^-, the sulphanilic acid - 1-naphthylamine method is used. For hydroxylamine, the soln. diluted with 25 ml of water is mixed with 0·5 ml of 0·05 *M* sulphanilic acid, heated at boiling-point for 5 to 6 min., cooled and then treated with 1·5 ml of 0·05 *M* sulphanilic acid and 1 ml of $\simeq$ 0·1 *N* iodine in glacial acetic

acid. After 5 min. the iodine is removed by 0·1 *N* $Na_2S_2O_3$ and, after a further 5 min., 1 ml of 0·035 *M* 1-naphthylamine is added and the NO_2^- formed from the hydroxylamine are determined. For NO_3^-, the soln. is treated directly with 0·3 ml of 0·05 *M* sulphanilic acid and 0·2 ml of $\simeq$ 0·1 *N* iodine. After 5 min. the soln. is boiled for 5 to 6 min., cooled and diluted to 20 ml. After 15 to 20 min. in ice the NO_3^- are reduced with zinc filings during 15 to 30 sec. Part (10 ml) of the filtered soln. is mixed with 25 ml of water, 2 ml of 0·05 *M* sulphanilic acid and 1 ml of $\simeq$ 0·1 *N* iodine. After 5 min., excess of iodine is removed by 0·1 *N* $Na_2S_2O_3$, and the NO_2^- formed from the NO_3^- are determined as above. The upper limiting concn. for the method are $1{\cdot}2 \times 10^{-6}$ *M* for NO_2^-, 5×10^{-7} *M* for hydroxylamine and 5×10^{-7} *M* for NO_3^-. G. S. SMITH

3911. **A new reagent for the colorimetric and spectrophotometric determination of phosphorus, arsenic and germanium.** F. Lucena-Conde and L. Prat (Univ. of Salamanca, Spain). *Anal. Chim. Acta*, 1957, **16** (5), 473–479.—A reagent containing Mo^{VI} and Mo^{V} yields a blue colour with PO_4^{3-} without the use of a reducing agent. *Reagent*—Dissolve 8·15 g of $(NH_4)_6Mo_7O_{24}.4H_2O$ in 60 ml of water. To 25 ml of this soln. add 12·5 ml of 12 *N* HCl and dilute to 50 ml; add 10 ml of Hg, shake for 5 min. and filter. To 30 ml of the initial soln. add 50 ml of 12 *N* HCl, 56 ml of 36 *N* H_2SO_4 and, with agitation, 40 ml of the reduced soln. This reagent is stable for 6 months. *Determination of phosphate*—To the test soln., containing up to 160 μg of P_2O_5, add 1·5 ml of the reagent, dilute with water to 30 ml and heat at 98° for 15 min. Allow to cool, dilute to 50 ml and determine the extinction spectrophotometrically at 840 mμ or with the use of a red filter. Interference arises from the presence of Ba^{2+}, Pb^{2+}, Bi^{3+} and Sb^{3+} which produce ppt.; SiO_3^{2-} (> 100 p.p.m.), AsO_4^{3-}, GeO_3^{2-} and WO_4^{2-} yield blue colours; Fe (> 20 p.p.m.), NO_3^- (> 20 p.p.m.) and oxalate (> 100 p.p.m.) reduce the sensitivity of the reaction. The analogous reactions with AsO_4^{3-} and GeO_3^{2-} have also been studied and have been found suitable for analytical application. W. C. JOHNSON

3912. **New rapid gravimetric method for the estimation of phosphate ion.** M. Vancea, C. Liteanu and M. Volușniuc. *Stud. Cercet. Chim., Cluj*, 1956, **7** (1–4), 101–110.—Bismuth phosphate is pptd. quant. at pH 0·6 to 0·7 in the presence of HNO_3; ions of Ca, Fe and Al do not interfere at this pH. The concn. of Bi should not exceed 5 g per litre. The ppt. is either calcined at 700° to 800° and weighed as $BiPO_4$, or filtered off in a crucible, washed with ethanol and ether, dried in a vacuum desiccator and weighed as $(BiPO_4)_3.H_2O$. The determination takes 1 hr. with calcining of the ppt., and only 30 min. by the use of a filter crucible. H. SHER

3913. **Gravimetric determination of phosphates as manganese ammonium phosphate.** S. K. Shushich. *Zb. Radova Polyoprivrednogo Fak. Univ. Beograd*, 1956, **2** (1), 195–212; *Ref. Zhur., Khim.*, 1957, Abstr. No. 23,473.—Neutralise the acid soln. of the phosphate ($> 5 \times 10^{-3}$ *M* P_2O_5) to phenolphthalein or bromothymol blue with aq. NH_3, add $(NH_4)_2SO_4$ (2 g) and hexamine (2 g), heat almost to b.p. and add dropwise a 1·5% soln. of $MnSO_4$ (20 ml for each 100 mg of P_2O_5) with const. stirring over a period of $\lt$ 15 min., and 5 ml of a 2% soln. of aq. NH_3 (or 2% aq. NH_3 dropwise to pH 7·6). Filter off the ppt., wash it first with 0·1% hexamine soln. to remove all SO_4^{2-} ($\simeq$ 350 ml for 100 mg of P_2O_5; test with $BaCl_2$), and then with 5 ml of 96% ethanol. Dry for 1 hr. at 105° and weigh as $MnNH_4PO_4.H_2O$. The error of the method is $\pm$ 2%. Pptn. at temp. $\lt$ 90° leads to large errors. C. D. KOPKIN

3914. **Determination of small amounts of arsenic in coal.** R. G. Ault and A. G. R. Whitehouse (Mitchells and Butlers, Ltd., Cape Hill Brewery, Birmingham). *J. Inst. Brewing*, 1956, **62** (5), 425–427.—The authors have simplified the method of Case (*J. Inst. Brewing*, 1938, **44**, 362). The finely powered coal (0·5 g) is intimately mixed with 0·5 g of a mixture of $KMnO_4$ and MgO (1:1) and transferred to a silica boat containing a thin layer of MgO. After being covered with MgO, the boat is placed in a silica combustion-tube and ignited in a stream of O for 5 min. after the coal has become incandescent. The ash is washed into a beaker, treated with 50% H_2SO_4 (2 ml) and 30% oxalic acid (2 ml) and boiled until a clear soln. is obtained. The As is then determined by the usual Gutzeit method. R. E. ESSERY

3915. **Rapid determination of arsenic in metallic acid-soluble substances.** H. Ploum and E. Schaefer. *Arch. Eisenhüttenw.*, 1956, **27** (10), 637–640.—The As is extracted by HNO_3 because of its strong oxidising properties. The later decomposition of the nitrate by drying, roasting at 300° and redissolving the oxide in HCl and $KClO_3$ is replaced in this quicker method by treatment with formic acid. The formation of (*a*) $Fe(OH)_3$ and (*b*) Br (if KBr has been added to promote distillation of $AsCl_3$) is inhibited by adding H_2SO_4 and H_3PO_4 to the HNO_3 solvent. After the evolution of NO_2 has ceased, $ZnCl_2$ is added, $AsCl_3$ is distilled off and estimated by potentiometric titration. In this titration, 30 to 50% by vol. of HCl on the vol. of soln. is necessary for accurate results. Good agreement with other methods was observed. F. J. M.

3916. **Organic co-precipitants (collectors). VII. Co-precipitation of bismuth. Determination of small amounts of bismuth in chromium - nickel base alloys.** V. I. Kuznetsov and L. I. Papushina. *Zhur. Anal. Khim.*, 1956, **11** (6), 686–688.—In the form of the complex anion BiI_4^-, Bi, even at dilutions of 1 μg in 100 ml, is quant. co-pptd. with methyl violet and completely separated from Ni, Cr and many other elements, but not from Cu, Sb and Sn. To determine Bi in chromium - nickel steel, the sample (1 to 4 g) is dissolved in HCl - HNO_3, evaporated, heated with H_2SO_4, and SiO_2 is removed. The filtrate is diluted to 700 ml (4-g sample) or 500 ml (2-g sample), neutralised to Congo red paper with aq. NH_3, and then treated with 3 ml of dil. H_2SO_4 for each 100 ml of soln. After additions for each 100 ml of 1 to 2 ml of 5% NH_4I or KI soln., 6 to 7 ml of $\simeq$ 1% methyl violet soln. and then 20 to 18 ml of 5% NH_4I or KI soln. to give a black ppt., the soln. is stirred for 3 min. and set aside for 1 to 2 hr. or overnight. The ppt. is collected on paper, washed with a mixture of 1 litre of 0·2 *N* H_2SO_4, 10 to 20 ml of 1% methyl violet soln. and 10 to 20 ml of 5% NH_4I or KI soln., ignited in a silica crucible after moistening of the slightly dried ppt. with HCl and H_2SO_4, and treated for removal

of Cu. For this, the soln. of the residue in HCl is mixed with 1 ml of 0·5% $AlCl_3$ soln. and the Al together with the Bi is pptd. by addition of aq. NH_3. The Bi is finally determined colorimetrically with KI and H_2SO_3. The method is suitable for determining contents of $\simeq$ 0·0005% and above.
G. S. SMITH

3917. **Micro-heterometric determination of bismuth with sodium diethyldithiocarbamate.** M. Bobtelsky and R. Rafailoff (The Hebrew Univ., Jerusalem, Israel). *Anal. Chim. Acta*, 1957, **16** (5), 488–492.—Bismuth ($\simeq$ 2 mg) is titrated by the heterometric method (*cf. Anal. Abstr.*, 1956, **3**, 12) with 0·0066 *M* Na diethyldithiocarbamate. An ammoniacal citrate or tartrate medium is used and the interference of certain metals is avoided by the addition of KCN or EDTA (disodium salt).
W. C. JOHNSON

3918. **Spectrochemical determination of small amounts of vanadium in samples of complex composition.** T. M. Moroshkina and V. K. Prokof'ev (A. A. Zhdanov Leningrad State Univ.). *Zhur. Anal. Khim.*, 1956, **11** (6), 714–716.—Samples of ores containing from 0·01 to 0·08% of V are specially prepared, together with similar samples containing known added amounts of V, by heating them in a reducing atmosphere in a special furnace to give compact masses which are then excited in a stabilised a.c. arc.
G. S. SMITH

3919. **Spectrophotometric study of aqueous solutions of quinquevalent vanadium.** Yu. V. Morachevskiĭ and L. I. Belyaeva (A. A. Zhdanov Leningrad State Univ.). *Zhur. Anal. Khim.*, 1956, **11** (6), 672–677.—The spectrophotometric behaviour of soln. of quinquevalent V over a wide range of pH is studied. At NaOH concn. of 0·5 to 0·1 *N* the reaction—

$$Na_3VO_4 + 2H_2O \rightleftarrows NaH_2VO_4 + 2NaOH$$

occurs. When the ratio [OH]:[V] becomes $\simeq$ 100:1 the predominating reaction is—

$$2NaH_2VO_4 \rightleftarrows Na_2H_2V_2O_7 + H_2O,$$

and when the ratio becomes $<$ 1 the reaction—

$$Na_2H_2V_2O_7 \rightleftarrows 2NaVO_3 + H_2O$$

commences. The latter reaction and the subsequent reactions—

$$NaVO_3 + H_2O \rightleftarrows NaOH + HVO_3$$

and—

$$NaVO_3 + HCl \rightleftarrows NaCl + HVO_3,$$

all give VO_3^-, the extinction of the soln. remaining unchanged between concn. of 10^{-5} *N* NaOH and 10^{-5} *N* HCl. When the ratio [V]:[H] becomes $\simeq$ 1:1, the reaction—

$$2HVO_3 \rightleftarrows H_2O + VO_2VO_3$$

commences and when the ratio becomes 1:100 the reaction—

$$VO_2VO_3 + 2HCl \rightleftarrows 2VO_2Cl + H_2O$$

has gone to completion. In very acid soln. the reaction—

$$VO_2Cl + 2HCl \rightleftarrows VOCl_3 + H_2O$$

takes place.
G. S. SMITH

3920. **Gravimetric determination of niobium in uranium - niobium alloys.** O. H. Kriege (Los Alamos Sci. Lab., N. Mex., U.S.A.). *U.S. Atomic Energy Comm.*, Rep. LA-2049, 1956, 14 pp.—The determination of Nb in U - Nb alloys is based on the pptn. of hydrated Nb_2O_5 from a H_2SO_3 soln. The sample is dissolved in HCl and H_2O_2, boiled to expel the excess of peroxide, and then treated with H_2SO_3. The ppt. is ignited at 800° and weighed as Nb_2O_5. A mean recovery of 100·46% with a standard deviation of $\pm$ 0·31% was obtained for 50 determinations on known soln. containing 30 to 60 mg of Nb and 0·5 to 6·0 g of U.
NUCLEAR SCI. ABSTR.

3921. **Spectrophotometric determination of tantalum with gallic acid.** H. Freund, K. H. Hammill and F. C. Bissonnette, jun. (U.S. Bureau of Mines, Albany, Oreg., U.S.A.). *U.S. Bur. Mines, Rep. Invest.*, 1956, No. 5242, 11 pp.—Gallic acid is a sensitive, stable, colorimetric reagent for the determination of Ta in the range of 2 to 40 μg of Ta per ml. The method consists in the fusion of Ta_2O_5 with $K_2S_2O_7$ and dissolution of the cooled melt in saturated ammonium oxalate soln., followed by development of a yellow complex with an ethanolic soln. of gallic acid. The Ta - gallic acid complex absorbs over a broad region in the blue and near u.v. Adverse effects due to interfering ions and soln. conditions, such as oxalate concn. and pH, can be minimised by a suitable choice of wavelength. Standard curves for determining Ta, analysing certain mixtures, and studying interferences are given.
CHEM. ABSTR.

3922. **Tantalum determination in presence of niobium by precipitation with N-benzoyl-N-phenylhydroxylamine[tantalon].** R. W. Moshier and J. E. Schwarberg (Wright Air Development Center, Wright-Patterson Air Force Base, Ohio, U.S.A.). *Anal. Chem.*, 1957, **29** (6), 947–951.—The sample containing $>$ 0·1 g of Ta_2O_5 is digested with HF, which is then removed by evaporation with H_2SO_4. The cooled residue is taken up in dil. HF and aq. N-benzoyl-N-phenylhydroxylamine is added to the soln. in a polyethylene beaker. The ppt. is filtered off at room temp., washed, and then ignited at 900°. The various conditions that affect the determination are discussed. An error of $\pm$ 0·2 mg is given. The pptn. must be repeated when large excesses of Zr, Ti and, especially, Nb are present, and the preliminary removal of Mo and W is recommended.
D. A. PANTONY

3923. **Gravimetric determination of tantalum in uranium - tantalum alloys.** O. H. Kriege and R. D. Gardner (Los Alamos Sci. Lab., N. Mex., U.S.A.). *U.S. Atomic Energy Comm.*, Rep. LA–2032, 1956, 20 pp.—Two gravimetric methods are described for the quant. determination of Ta in U - Ta alloys. In the first procedure, the sample is dissolved in HNO_3 and HCl, fumed to dryness with H_2SO_4, taken up with water and treated with H_2SO_3 to precipitate hydrated Ta_2O_5. The ppt. is ignited at 1000° and weighed as Ta_2O_5. A mean recovery of 100·2% with a standard deviation of $\pm$ 0·6% was obtained for 33 determinations on known soln. containing 30 to 45 mg of Ta and 3 to 6 g of U. In the second method, the sample is dissolved with HNO_3 and HF, fumed to dryness with H_2SO_4, taken up with water and treated with cupferron in a strongly acid soln. to precipitate the Ta. Sulphurous acid is added before the pptn. with cupferron to reduce any Fe that may be present. The ppt. is ignited at 1000° and weighed as Ta_2O_5. A mean of 100·3% was found with a mean standard deviation of $\pm$ 0·6% for 35 determinations on known soln. containing amounts of Ta and U as in the first method.
NUCLEAR SCI. ABSTR.

3924. **Solvent extraction of protactinium with phosphate esters.** A. J. Fudge and J. L. Woodhead (A.E.R.E., Harwell, England). *Chem. & Ind.*, 1957, (33), 1122.—In the preparation of fissile ^{233}U from Th, it is usual to commence the separation of the Th and U before the whole of the second intermediate product, ^{233}Pa, has decayed into ^{233}U. Conventional solvent procedures are used, and experiment has shown that, although the agent used is commercial tributyl phosphate, the actual active agent is dibutyl phosphate present in small quantities. It has been shown experimentally that the influence of the acidity of the ^{233}Pa solution is very small. By using an intermediate stage of separation by pptn. with niobium compounds, and subsequent separation of the Nb and Pa by the dibutyl phosphate, carrier-free ^{233}Pa can be obtained from irradiated thoria, and the process appears to be a prospective method of quantitative analysis for ^{233}Pa in irradiated Th, or for ^{231}Pa in uranium residues. J. F. P. H. GREENE

3925. **Isotopic method for determining oxygen in chromium.** A. D. Kirshenbaum (Research Inst., Temple Univ., Philadelphia, Pa., U.S.A.). *Anal. Chem.*, 1957, **29** (6), 980–981.—The sample is heated at 1400° to 1500° with a known amount of chromium metal powder, containing a known proportion of ^{18}O, in an apparatus from which the gases are examined by mass-spectrometry. A deviation of 0·73% of the oxygen content is given, and the method is very rapid. D. A. PANTONY

3926. **Rapid analysis of refined sulphur. I. Decomposition of the sample and colorimetric determination of selenium.** Fumio Aoki and Teru Yuasa (Gov. Chem. Ind. Res. Inst., Yoyogi P.O., Tokyo). *Rep. Gov. Chem. Ind. Res. Inst., Tokyo*, 1956, **51** (11), 415–418.—Selenium dioxide is quant. reduced with KI in 0·5 to 3 *N* HNO_3, the iodine being decolorised with $SnCl_2$. The extinction coeff. at 430 mμ of the resulting soln. is proportional to the amount of Se up to 200 μg per 50 ml. Comparable amounts of Te interfere with the colorimetry, but its content in refined sulphur is negligible. The sample (30 g) is slowly ($\simeq$ 2·5 hr.) ignited in a current of O ($\simeq$ 200 ml per min.). The inside wall of the combustion tube is rinsed with warm dil. HNO_3 ($\simeq$ 100 ml) and then with water. A portion (10 to 25 ml) of the combined washings (500 ml) is diluted to $\simeq$ 45 ml, reduced with 5% KI soln. (3 ml) for 10 min., treated with 10% $SnCl_2$ soln. (5 drops) and made up to 50 ml. The results compare favourably with those obtained by gravimetric analysis. The time taken for an estimation is $\simeq$ 4 hr.

II. Determination of arsenic. Fumio Aoki. *Ibid.*, 1956, **51** (11), 419–422.—Arsenic (0·003 to 0·03% in refined sulphur), quant. collected in the HNO_3 washings, is distilled as AsH_3 into dil. iodine soln. containing $NaHCO_3$ and colorimetrically determined by the molybdenum blue method. The effect of interfering elements, including Ge, P and Si, is negligible. K. SAITO

3927. **Determination of sulphuric acid in copper electroplating baths with the sodium carbonate - methyl orange reagent.** L. Moore. *Chem. & Ind.*, 1957, (27), 951–952.—The quality of the deposit depends on the composition of the bath being fairly constant at about 20% $CuSO_4.5H_2O$ and 8% w/v H_2SO_4. This is checked in the workshop by checking specific gravity with a hydrometer to give total concn. and titrating H_2SO_4 with NaOH soln. so that the vol. (ml) of NaOH taken $\equiv$ oz per gall. of H_2SO_4. The end-point is indicated by a slight permanent turbidity, but the $Cu(OH)_2$ is less readily soluble in dil. H_2SO_4 as the end-point is approached and prolonged shaking is necessary. When NaOH is replaced by Na_2CO_3, the end-point is sharper ($CuCO_3$ is more soluble), and methyl orange, which gives a pure grey end-point, can be used as indicator. F. J. M.

3928. **Determination of tervalent chromium in the presence of chromate.** R. W. Cline, R. E. Simmons and W. R. Rossmassler (Union Carbide Nuclear Co., Paducah, Ky., U.S.A.). *U.S. Atomic Energy Comm.*, Rep. KY–173, 1956, 6 pp.—A method is described for the determination of small amounts of Cr^{III} in H_2O containing $\simeq$ 300 p.p.m. of chromate. The Cr^{III} is pptd. from the chromate by aq. NH_3 by using $Al(OH)_3$ as carrier, oxidised to chromate with Br and determined spectrophotometrically. The method covers the range of 0 to 0·5 p.p.m. of Cr^{III}, but can be extended. CHEM. ABSTR.

3929. **Detection and colorimetric determination of the CrO_4^{2-} ion with o-dianisidine.** F. Buscarón and J. Artigas (Univ. of Barcelona, Spain). *Anal. Chim. Acta*, 1957, **16** (5), 452–454.—A soln. of *o*-dianisidine is prepared by dissolving 1 g in 2 ml of hot conc. acetic acid and diluting to 100 ml with water. A few drops of this soln. added to a soln. of CrO_4^{2-} produce a blue colour or ppt. On acidifying to pH < 2·8, a red soln. is obtained. In a micro test-tube the dilution limit is $10^{-6\cdot3}$; on a filter-paper it is $10^{-5\cdot3}$. A similar colour is obtained with Fe^{3+}, Au^{3+}, Ce^{4+}, OsO_4^{2-}, VO_3^- and $Fe(CN)_6^{3-}$. The sensitivity is decreased by Sb, Sn and Pt. The following are tolerated in a 100:1 ratio—Pb, Bi, Cd and As, while Al, Cr^{3+}, Ni, Co and Zn do not interfere. For quant. tests, 0·5 ml of the reagent soln. and 2 ml of 2 *N* H_2SO_4 are added to the test soln., which is then diluted with water to 25 ml. After 5 min. the extinction at 450 mμ is determined. W. C. JOHNSON

3930. **Direct determination of chromium in chromium-containing iron ore by means of sintering.** Yu. I. Usatenko and E. A. Klimkovich (Chem. Technol. Inst., Dnepropetrovsk). *Ukrain. Khim. Zhur.*, 1956, **22**, 670–672.—Decomposition of Cr-bearing ironstone is accomplished by fusing 0·2 g of finely ground sample either with 0·6 g of soda lime and 0·4 g of Na_2CO_3 or with 0·4 g of MgO and 0·4 g of Na_2CO_3, at 1100° for 15 min., and dissolving the melt in 25 ml of HCl (1:1) or in 40 ml of H_2SO_4 (1:4) when MgO is used. Under these conditions all of the Cr is in the sexavalent state and can be titrated directly. CHEM. ABSTR.

3931. **[Comparison of] various methods for the volumetric determination of molybdenum.** E. V. Ankudinova and V. I. Petrashen'. *Trudy Novocherkas. Politekh. Inst.*, 1956, **41** (55), 3–10; *Ref. Zhur., Khim.*, 1957, Abstr. No. 23,438.—The volumetric methods are studied by using materials with a high content of Mo. It is concluded that methods based on the reduction of Mo^{VI} to Mo^{V} with metallic mercury, bismuth amalgam and metallic bismuth give better results than methods based on the reduction of Mo^{VI} to Mo^{III} with amalgamated zinc in a Jones reductor and with zinc amalgam. C. D. KOPKIN

3932. **New aromatic amines as reagents for tungsten. II. 4:4′-Diamino-3:3′-dimethyltriphenylmethane.** F. Lucena-Conde and J. Zato (Anal. Chem. Lab., Univ. Salamanca). *An. Real Soc. Esp. Fis. Quim.*, 1956, **52** (5), 353–358.—The preparation of 4:4′-diamino-3:3′-dimethyltriphenylmethane (**I**) is described. In *N* acetic acid the reagent [a 3% (w/v) soln. in dil. HCl] gives a ppt. of composition $4WO_3.C_{12}H_{22}N_2.xH_2O$, but this is liable to be contaminated with **I**. Molybdenum gave a similar ppt. but it was not quant. at any pH.

III. Practical applications of the proposed new reagents. J. Zato and F. Lucena-Conde. *Ibid.*, 1956, **52** (5), 319–324.—The effect has been studied of different interfering substances on the recovery of W when it is pptd. by **I** or by 4:4′-diaminotriphenylmethane (**II**) (*cf. Anal. Abstr.*, 1956, **3**, 1342) in comparison with benzidine and cinchonine. The sample is fused with Na_2CO_3 and K_2CO_3, and the soln. made slightly acid to methyl orange with HCl. The ppt. with either **I** or **II** is filtered off, washed, and ignited to WO_3. The error is $< 0{\cdot}1\%$ of the W present. The ppt. with **I** is more easily collected and filtered. R. L. Mortlock

3933. **Determination of small quantities of tungsten in ores.** A. F. Nemirovskaya. *Trudy Novocherkas. Politekh. Inst.*, 1956, **41** (55), 23–25; *Ref. Zhur., Khim.*, 1957, Abstr. No. 23,441.—To 0·5 or 1 g of scheelite ore add 3 to 4 ml of a mixture of conc. HCl and HNO_3; evaporate to dryness, moisten the residue with conc. HCl, add 5 ml of water, heat until dissolved, and filter off H_2WO_4 and H_2SiO_3. Wash the ppt. with a 5% NH_4NO_3 soln. till free of Fe and treat it with 25 ml of a 10% soln. of aq. NH_3 on a water bath for 20 to 30 min. Add 5 ml of magnesia mixture, filter and wash the ppt. Evaporate the filtrate and wash liquors to dryness and ignite to remove NH_4^+. Add to the residue a little warm 5% NaOH soln., filter, wash the ppt. with hot 0·5% alkali soln., and dilute to 100 ml with water. Neutralise 0·1 to 2 ml to phenolphthalein with 0·05 *N* HCl, add 0·05 ml of 0·5 *N* HCl, mix, and after 5 min. add 1 ml of a 0·01% soln. of methyl violet (total vol. 5 ml). Mix the soln. and compare the colour with a standard scale prepared from a titrated soln. of Na_2WO_4. The accuracy of the method is 0·2% with a content of W of 1·6%. The method may be used for the analysis of ores containing up to 10% of Mo and large quantities of P and Si. C. D. Kopkin

3934. **Spectrophotometric determination of tungsten in tantalum, titanium and zirconium using dithiol.** P. Greenberg (Electrometallurgical Co., Niagara Falls, N.Y., U.S.A.). *Anal. Chem.*, 1957, **29** (6), 896–898.—The method can be used to determine 0·01 to 0·2 mg of W. After dissolving the sample in dil. HF, W is reduced with titanium sponge or Ti^{III} soln. Quinquevalent W reacts with dithiol to form a blue-green complex, which is extractable with amyl acetate and has max. extinction at 640 mμ. Six samples can be analysed in 2·5 to 3 hr. Five portions of a sample containing 0·095 mg of W in titanium were analysed and an average of 0·096 mg was recovered, with a max. difference of 0·003 mg. K. A. Proctor

3935. **Activation analysis of trace impurities in tungsten using scintillation spectrometry.** J. F. Cosgrove and G. H. Morrison (Sylvania Electric Products Inc., Flushing, N.Y., U.S.A.). *Anal. Chem.*, 1957, **29** (7), 1017–1019.—The sensitive, quant. method is based on the use of activation by thermal neutrons. After the separation of radioactive W by pptn. with benzoin α-oxime, impurities are identified and measured by gamma scintillation spectrometry. The method is sensitive to 0·001 to 1 μg for many elements. The precision was never worse than a coeff. of variation of 10%, but the accuracy was low by as much as 30% in some cases. K. A. Proctor

3936. **Estimation of tungstate ion by tensammetry.** B. Breyer and S. Hacobian (Univ. of Sydney, Australia). *Anal. Chim. Acta*, 1957, **16** (5), 497–500.—Tungstate ions are determined by the same experimental technique as that used for a.c. polarography, but the underlying process differs from polarography in that no electron transfer takes place at the electrode and thus no d.c. polarographic steps are obtained. The a.c. is produced by the absorption-desorption processes at the electrode-soln. interface. The name "tensammetry" is applied to the principle used. W. C. Johnson

3937. **Volumetric determination of uranium. Titanous sulphate as reductant before oxidimetric titration.** J. S. Wahlberg, D. L. Skinner and L. F. Rader, jun. (U.S. Geological Survey, Denver, Colo., U.S.A.). *Anal. Chem.*, 1957, **29** (6), 954–957.—The sample, containing approx. 50 mg of U, is dissolved in boiling H_2SO_4-$HClO_4$-HNO_3-HF mixture and the soln. is evaporated to fumes of H_2SO_4. The residue is diluted with water and treated with boric acid and $KMnO_4$, followed by cupferron in a special rapid-filtration apparatus. The ppt. is filtered off and washed, and the filtrate is evaporated to fumes of H_2SO_4 in the presence of HNO_3 and $HClO_4$. After extraction with water and filtration if necessary, the soln. is treated with a little Cu^{2+} and then sufficient excess of $Ti_2(SO_4)_3$ to produce a ppt. of metallic Cu. Excess of Ti^{3+} is destroyed by addition of $Hg(ClO_4)_2$ soln. and, at the disappearance of the metallic Cu, $Fe_2(SO_4)_3$ and ferroin indicator are added and the soln. is titrated with standard $Ce(SO_4)_2$ soln. A reagent-blank titration is carried out. Selenium interferes and must be removed by a preliminary treatment. A standard deviation of ± 0·0034% on samples containing 0·2 to 0·4% of U is given. D. A. Pantony

3938. **Coulometric determination of uranium(VI) at controlled potential.** G. L. Booman, W. B. Holbrook and J. E. Rein (Phillips Petroleum Co., Idaho Falls, U.S.A.). *U.S. Atomic Energy Comm.*, Rep. IDO–14369, 1956, 7 pp.—Small amounts of U^{VI} are reduced to U^{IV} in 5 to 10 min. at a mercury cathode with controlled potential electrolysis. The reaction is followed coulometrically and accurate results may be obtained for 0·75 to 75 mg of U. There is no interference from Hg, Cu, Al, Fe and large amounts of HNO_3 when either a potassium citrate-aluminium sulphate or H_2SO_4 electrolyte is used. In citrate media the reduction potential was limited to − 0·60 V *vs.* the Ag-AgCl-KCl electrode. The method is especially useful in the analysis of soln. obtained during the recovery of U from spent fuel elements. Chem. Abstr.

3939. **Rapid spectrophotometric determination of submilligram quantities of uranium.** C. A. Francois (Dow Chem. Co., Western Div., Pittsburg, Calif., U.S.A.). *U.S. Atomic Energy Comm.*, Rep. DOW–150, 1956, 36 pp.—A simple colorimetric method for U involving solvent extraction of UO_2^{2+} from $Al(NO_3)_3$

soln. with tributyl phosphate (**I**) in *iso*octane is described. An aliquot of the **I** - *iso*octane - uranium mixture is introduced into an acetone - water soln. of dibenzoylmethane and the resulting complex is measured spectrophotometrically at 410 mμ. There is no interference from common cations except Th, and precision is good.

NUCLEAR SCI. ABSTR.

3940. **Spectrophotometric determination of uranium in highly impure solutions.** R. B. Kimball and J. E. Rein (Phillips Petroleum Co., Idaho Falls, U.S.A.). *U.S. Atomic Energy Comm.*, Rep. IDO–14380, 1956, 14 pp.—The acetone - thiocyanate method of Crouthamel and Johnson (*Anal. Chem.*, 1952, **24**, 1780) was modified by addition of a preliminary extraction with 5% tributyl phosphate in CCl_4 and by substitution of 95% ethanol for acetone in the thiocyanate reagent; this improved the stability and eliminated the necessity of stripping the org. phase. Approximate tolerance limits for 94 impurities were determined. Compared to the unmodified procedure the method showed as high or higher tolerances for most cations and many anions, but showed lower tolerances for anions that complex with U^{VI} and thus inhibit quant. extraction.

CHEM. ABSTR.

3941. **Spectrophotometric determination of uranium by 2-acetoacetylpyridine.** Tadashi Hara (Fac. of Engng, Doshisha Univ., Karasuma, Kamigyo-ku, Kyoto). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1957, **78** (3), 333–337.—2-Acetoacetylpyridine (**I**) was synthesised by the action of Na on a mixture of the ethyl ester of pyridine-2-carbcxylic acid, acetone and ether and dissolved in butyl acetate (**II**) (300 mg per 250 ml). The uranyl complex of **I** is extracted into the **II** layer from a neutral soln. (pH 7·0 to 7·7) containing the acetate. The yellow soln. shows a max. absorption at 382·5 mμ, when the extinction is measured *vs.* the reagent soln. The presence of CO_3^{2-}, PO_4^{3-}, $B_4O_7^{2-}$, V, Ti, Cu and a large amount of Al causes interference with the extraction of the uranyl complex. The working curve is linear for < 300 μg of U per 10 ml of **II**. The molar ratio of **I** in **II** to U in the aq. layer must be > 160. This method is an improvement on the dibenzoylmethane method (*cf.* Yeo *et al.*, *Anal. Abstr.*, 1954, **1**, 80). Separation of U from interfering ions is achieved by a new column extraction method (*Anal. Abstr.*, 1957, **4**, 3942).

K. SAITO

3942. **Separation of uranium by column extraction and its spectrophotometric determination.** Tadashi Hara (Fac. of Engng, Doshisha Univ., Karasuma, Kamigyo-ku, Kyoto). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1957, **78** (3), 337–340.—The use of an adsorption column of SiO_2 is proposed for the complete separation of U from Th, PO_4^{3-}, Al, Zr, rare-earth elements and heavy metals. Uranium nitrate (50 to 500 μg) in 20% HNO_3 (1 ml) is mixed with anhydrous Na acetate (0·9 g) and ignited SiO_2 (1·5 g); if Th (< 25 mg) and PO_4^{3-} (< 30 mg) are present, Na oxalate (60 mg) and Fe^{3+} (100 mg) are added to this mixture. A mixture (4 g) of SiO_2 and $NaNO_3$ (4 + 1) is placed on glass wool in a separating funnel, and wetted with ether containing 1% HNO_3; the sample mixture is added, covered with SiO_2 (0·5 g) and the column is eluted ($<$ two drops per 3 sec.) with ether (150 ml) containing 1% HNO_3. The U in the eluate is extracted with water (3 × 10 ml). The aq. layer is evaporated and submitted to spectrophotometry with 2-acetoacetylpyridine (*Anal. Abstr.*, 1957, **4**, 3941).

K. SAITO

3943. **Spectrophotometric estimation of uranium with tiron.** B. Sarma and C. P. Savariar (Nat. Chem. Lab., Poona, India). *J. Sci. Ind. Res., B, India*, 1957, **16** (2), 80–82.—*Procedure*—The soln. containing U is placed in a 25-ml flask and treated with tiron reagent (5% aq. soln. w/v) (5 ml) and Na acetate (10% aq. soln. w/v) (5 ml), the pH is adjusted to 3, and the vol. made up to 25 ml with water. The extinction of the soln. is read at 373 mμ and the U is calc. from a standard curve. The complex obeys Beer's law for concn. up to 400 p.p.m.

C. A. SLATER

3944. **Spectrophotometric determination of uranium in ores.** H. I. Feinstein (U.S. Geol. Survey, Washington, D.C., U.S.A.). *U.S. Atomic Energy Comm.*, Rep. TEI–555, 1955, 16 pp.—The yellow complex of U^{VI} with thiocyanate is used for the spectrophotometric determination of U in ores following extraction with ethyl acetate. Control of acidity and SCN^- concn. is requisite for accurate results. The procedure involves ashing, dissolving of the ash in 7% HNO_3, extraction with ethyl acetate in the presence of $Al(NO_3)_3$, water stripping, and colour development with $SnCl_2$, acetone and NH_4SCN. The extinction is measured at 375 or 420 mμ, according to the final concn. of U. Results are reported for a number of V-containing ores.

CHEM. ABSTR.

3945. **Differential spectrophotometric determination of uranium and niobium.** C. V. Banks, K. E. Burke, J. W. O'Laughlin and J. A. Thompson (Iowa State Coll., Ames, U.S.A.). *Anal. Chem.*, 1957, **29** (7), 995–998.—The procedure described has been used for the analysis of alloys containing 90% of U, but is adaptable to most binary alloys of U and Nb. Uranium is determined by measuring the absorbance of a soln. of U^{VI} in 50% H_2SO_4 at 420 mμ against a reference soln. Niobium does not interfere and is itself determined by measuring the absorbance of a soln. of the complex formed with H_2O_2 in H_2SO_4. Under these conditions the max. absorbance of perniobic acid occurs at 360 mμ. Because U^{VI} has an absorbance at this wavelength, a correction is made by subtraction from the observed absorbance.

K. A. PROCTOR

3946. **The use of trialkylphosphine oxides as extractants in the fluorimetric determination of uranium.** J. C. White (Oak Ridge Nat. Lab., Tenn., U.S.A.). *U.S. Atomic Energy Comm.*, Rep. ORNL–2161, 1956, 30 pp.—Tri-*n*-octyl- and tri-*n*-decyl-phosphine oxides were shown to be excellent extractants for U in its fluorimetric determination. These phosphine oxides quant. extract U from soln. that are as conc. as 12 *M* with respect to such acids as H_2SO_4, H_3PO_4 and HCl. The extraction is also quant. in the presence of such anions as citrate, oxalate and tartrate that form strong complexes with the UO_2^{2+} in soln. *Procedure*—Add 5 ml of 6 *M* HNO_3 to a 1-ml aliquot of the sample, and then shake for 5 min. with 5 ml of 0·1 *M* trialkylphosphine oxide in Varsol (a kerosene-type mixture of aliphatic hydrocarbons). A detailed procedure is presented for the prep. of tri-*n*-octylphosphine oxide.

NUCLEAR SCI. ABSTR.

3947. **The X-ray spectrometric determination of uranium in solution.** D. S. Flikkema, R. P. Larsen and R. V. Schablaske (Argonne Nat. Lab., Lemont, Ill., U.S.A.). *U.S. Atomic Energy Comm.*, Rep. ANL–5641, 1956, 10 pp.—An X-ray spectrometric method has been developed for the determination of milligram quantities of U in soln. In speed, sensitivity and accuracy it is comparable with spectrophotometric methods. Its freedom from interferences other than gross concn. of other elements makes it notably superior for many applications.
NUCLEAR SCI. ABSTR.

3948. **Separation and determination of neptunium by liquid - liquid extraction.** F. L. Moore (Oak Ridge Nat. Lab., Tenn., U.S.A.). *Anal. Chem.*, 1957, **29** (6), 941–944.—The soln. of Np is made *M* with respect to HCl and hydroxylamine hydrochloride and 0·25 *M* with respect to $FeCl_2$ (or 2 *M* to KI) and, after warming to reduce the element to Np^{IV}, the soln. is cooled and extracted with an equal vol. of 0·5 *M* 2-thenoyltrifluoroacetone in xylene. The org. layer is washed with *M* HCl and the Np^{IV} is back-washed with 10 *M* HNO_3: at this stage radioactive Zr and Pa can be removed by a further extraction with 2-thenoyltrifluoroacetone, into which Np^{VI} is not extracted. The Np^{VI} in the aq. phase is determined by standard radiochemical methods. Most fission products cause no interference, but the presence of SO_4^{2-}, PO_4^{3-}, F^- and oxalate leads to low results.
D. A. PANTONY

3949. **Chromatographic detection of mixed halide ions in 10^{-10}-gram particles.** N. H. Farlow (U.S. Naval Radiological Defense Lab., San Francisco, Calif., U.S.A.). *Anal. Chem.*, 1957, **29** (6), 881–883.—Soluble chlorides, bromides and iodides are pptd. at 70° as silver salts in a gel which contains $Ag_2Cr_2O_7$. Owing to different solubilities, the silver halides appear as concentric rings, the iodide innermost. The I^-, Br^- and Cl^- are recognised by location with, respectively, u.v. irradiation, gaseous NH_3 and water vapour. The size of the rings is a semi-quant. estimate of the halide concn. The limit of detection of any ion in any triple mixture is said to be 5×10^{-11} g.
D. A. PANTONY

3950. **Detection of fluorine with ferric thiocyanate.** E. Vrotek, A. I. Pozigun and S. Pokraka. *Trudȳ Odessk. Univ., Ser. Khim. Nauk*, 1956, **146** (5), 115–119; *Ref. Zhur., Khim.*, 1957, Abstr. No. 23,489.—The conditions are studied for the detection of F^- by the decolorising of $Fe(SCN)_3$. The limiting dilution is 1 in 1×10^5; the limit of detection is 0·01 mg per ml. The following anions do not cause interference—Cl^-, ClO^-, ClO_3^-, ClO_4^-, Br^-, BrO^-, BrO_3^-, I^-, IO_3^-, IO_4^-, CN^-, SCN^-, NO_2^-, NO_3^-, S^{2-}, SO_3^{2-}, $S_2O_3^{2-}$, SO_4^{2-}, $S_2O_8^{2-}$, AsO_2^-, AsO_3^{3-}, AsO_4^{3-}, CO_3^{2-}, BO_3^{3-}, SiO_3^{2-}, $[Fe(CN)_6]^{3-}$, $[Fe(CN)_6]^{4-}$, PO_4^{3-}, PO_2^-, PO_3^{3-}, $P_2O_7^{4-}$, MnO_4^-, CrO_4^{2-}, $Cr_2O_7^{2-}$, CH_3COO^-, $C_2O_4^{2-}$, $HCOO^-$, and anions of the oxy acids of the aliphatic series.
C. D. KOPKIN

3951. **Determination of fluorine by the alizarin - zirconium complex in the presence of phosphate ions. Application to natural phosphates.** R. Vigier (Centre d'Études et de Recherches, Comptoir des Phosphates, N. Africa). *Bull. Soc. Chim. France*, 1957, (2), 160–167.—A study has been made of various coloured complexes for the estimation of F. The system F - alizarin - Zr - H_3PO_4 has been found to be very satisfactory because of the absence of interference by other substances, and it has been applied to the estimation of F in naturally occurring phosphates. *Procedure*—The sample to be analysed (100 mg; finely powdered) is fused for 5 min. in a platinum crucible with a mixture of Na_2CO_3 and K_2CO_3 (1:1 w/w) (1 g). The product is dissolved in 20% HCl (100 ml) and the soln. is transferred to a 500-ml flask and made up to vol. with water. A 10-ml aliquot is transferred to a 100-ml flask and 20% HCl ($\simeq$ 25 ml) is added, followed by the reagent (20 ml), which is prepared as described below, and then water (to 100 ml). A series of standard soln. are made up containing F^- (250 to 0 μg) as NaF, a soln. containing $(NH_4)H_2PO_4$ (97 mg), $CaCO_3$ (178 mg), Na_2CO_3 (1 g), K_2CO_3 (1 g), 20% HCl (200 ml) and water (to 1 litre) (10 ml), reagent soln. (20 ml) and water (to 100 ml). After 1 hr., the soln. are measured spectrophotometrically at 520 mμ. *Reagent. Soln.* (*i*)—Sodium alizarin-sulphonate (2 g) in water (1 litre). *Soln.* (*ii*)—Zirconium nitrate (2 g) is treated with water (200 to 300 ml), HCl (sp. gr. 1·19; 100 ml) is added, and the soln. made up to 1 litre with water. The reagent is prepared by mixing soln. (*ii*) (100 ml) with HCl (100 ml), diluting to 500 ml with water, and adding soln. (*i*) (75 ml). This soln. is stable for about 1 week.
C. A. SLATER

3952. **Synthetic mica investigations. VII. Chemical analysis and calculation to unit formula of fluorosilicates.** H. R. Shell and R. L. Craig (U.S. Bur. Mines, Norris, Tenn., U.S.A.). *U.S. Bur. Mines, Rep. Invest.*, 1956, No. 5158, 30 pp.—The general aim was to investigate or develop methods of analysis for fluorosilicates that would give a high order of accuracy with a min. of operations. An accuracy of $\pm$ 0·1% on the original sample basis was set as the max. deviation desirable. The report discusses factors affecting the determination of silica, distilling apparatus, and procedure, titration of F^- with $Th(NO_3)_4$, the effect of various ions on recovery of F^- by distillation as fluorosilicic acid, determination of F^- by distillation in the presence of borates, detailed procedure for determining F and SiO_2 by the Zn - Na_2CO_3 fusion method, notes on the determination of other constituents in mica, and results for SiO_2 by the ZnO fusion procedure.
CHEM. ABSTR.

3953. **Quantitative determination of chloride ion in 10^{-6} to 10^{-12}-gram particles.** N. H. Farlow (U.S. Naval Radiological Defense Lab., San Francisco, Calif., U.S.A.). *Anal. Chem.*, 1957, **29** (6), 883–885.—A gelatin film impregnated with $Ag_2Cr_2O_7$ is prepared by a rigidly standardised technique and the Cl^--containing particles are collected on it. After exposure to water vapour at 70°, the Cl^- concn. is estimated by either measurement of the clear spots due to AgCl and comparison with spots due to standard sodium chloride crystals or from a knowledge of the $Ag_2Cr_2O_7$ concn. The error associated with the production of the calibration procedures is discussed.
D. A. PANTONY

3954. **A new spectrophotometric method for the determination of small amounts of chloride using the mercuric thiocyanate method.** Iwaji Iwasaki, Satori Utsumi, Ken Hagino and Takejiro Ozawa (Lab. of Anal Chem. and Geochem., Tokyo Inst. of Technol.). *Bull. Chem. Soc. Japan*, 1956, **29** (8), 860–864.—The rapid colorimetric method for the determination of small quantities of Cl^- described previously (*Bull. Chem. Soc. Japan*, 1952, **25**, 226) has been modified so that Beer's law is now obeyed.

Interference is caused by Br^-, I^-, CN^-, SCN^-, S^{2-}, $S_2O_3^{2-}$, BrO_3^-, $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$. The error is $< \pm 1\%$ for the range of 5 to 80 p.p.m. of Cl^- and $< \pm 0{\cdot}05$ p.p.m. for the range 0·05 to 5 p.p.m. of Cl^-. *Procedure*—For the range 5 to 80 p.p.m. of Cl^-, mix the sample (2·5 ml) with a soln. of ferric alum (80 mg) in 6 *N* HNO_3 (1 ml) and a 0·1% soln. of $Hg(SCN)_2$ in dioxan - ethanol (9:1) (3 ml) and after 10 min. measure the extinction at 460 mμ. For the range 0·05 to 5 p.p.m. of Cl^-, mix the sample (5 ml) with ferric alum soln. (1 ml) and a 0·1% soln. of $Hg(SCN)_2$ in dioxan - ethanol (2:1) (1·5 ml) and measure the extinction at 460 mμ.

A. R. ROGERS

3955. **Quantitative determination of hypochlorites with Rhodamine B.** R. L. Dremlyuk and N. M. Stashko. *Trudȳ Odessk. Univ., Ser. Khim. Nauk*, 1956, **146** (5), 55–58; *Ref. Zhur., Khim.*, 1957, Abstr. No. 23,493.—A titrimetric semi-micro method is evolved for the determination of ClO^- in concn. of 0·01 to 0·001 *N*, with Rhodamine B. Acidify a standard Rhodamine B soln. (20 ml) with *N* H_2SO_4 (5 ml) and titrate with the hypochlorite soln. till decolorised. The method may be used in the presence of ClO_3^-. C. D. KOPKIN

3956. **Polarographic determination of bromine ion.** L. Kékedy, F. Mánok and I. Albu. *Stud. Cercet. Chim., Cluj*, 1956, **7** (1–4), 61–67.—The method is based on quant. oxidation of Br^- to BrO_3^- by NaOCl in the presence of acetate buffer at pH 7·5. After extraction and elimination of O by a current of H, the polarographic determination is made. Iodides, when present, are first oxidised to iodine by H_2O_2 in the cold, and the iodine is extracted with chloroform. An accuracy of $\pm 2\%$ is given on quantities of Br of about 100 μg in the presence of 2 mg of Cl. The method is recommended for the determination of Br in mineral waters, and small samples (50 to 200 ml) can be analysed rapidly.

H. SHER

3957. **Determination of carbon in bromine.** M. Codell and G. Norwitz (Pitman-Dunn Lab., Frankford Arsenal, Philadelphia, Pa., U.S.A.). *Anal. Chem.*, 1957, **29** (6), 967–969.—An apparatus is described in which the bromine sample is heated with O at 1000° to convert carbon compounds into CO_2, which is freed from Br in a solid CO_2 trap and then purified by passage through $CuSO_4$, MnO_2 and $Mg(ClO_4)_2$ before absorption in soda lime and weighing. A 10-ml sample is used. Accuracy data are presented. D. A. PANTONY

3958. **The iodate - iodide - acid system used for conductimetric titration of iodates and strong acids.** D. Ceauşescu and C. Petrescu. *Stud. Cercet. Chim., Cluj*, 1956, **7** (1–4), 81–84.—Experiments show that the system—

$$IO_3^- + 5I^- + 6H^+ \rightleftarrows 3I_2 + 3H_2O$$

permits conductimetric determination of IO_3^- in the presence of an excess of I^- by titration with a strong acid, and determination of a strong acid in the presence of excess of I^- by titration with IO_3^-. The presence of an excess of I^- ensures that the reaction is complete. In both cases the curves show sharp inflections at the end-points.

H. SHER

3959. **Separation of inorganic mixtures by partition. XIV. The partition of poly-iodides between aqueous solutions and organic solvents.** R. Bock and T. Hoppe (Farbwerke Hoechst A.-G., Frankfurt-am-Main). *Anal. Chim. Acta*, 1957, **16** (5), 406–415.—When aq. soln. containing alkali-metal halides and iodine are extracted with nitromethane the proportion of alkali-metal salt extracted increases with increasing iodine concn. The proportion also increases on changing the metal radicals in the order Li, Na, K, Rb, Cs, and on changing the anions in the order Cl, F, Br, I. Nitromethane, nitrobenzene and diethyl ether afford no satisfactory separations of the salts, but a mixture of nitromethane and benzene gives a high separation factor for KI and RbI. A soln. containing iodine and KOCN or KSCN also yields a high proportion of salt to nitromethane. W. C. JOHNSON

3960. **Colorimetric estimation of manganese.** W. V. Single (Res. Inst. of Plant Physiology, Imp. Coll. of Sci. and Technol., London). *Nature*, 1957, **180**, 250–251.—The results of a preliminary investigation of the reaction between tetramethyldiaminodiphenylmethane ("tetrabase") and Mn in trace quantities are discussed. G. S. ROBERTS

3961. **The paper chromatography of some manganese and copper valency states.** H. M. Stevens (Long Ashton Res. Station, Univ. of Bristol, England). *Anal. Chim. Acta*, 1957, **16** (5), 435–438.—Chromatographic separations on paper strips are described for Mn^{2+} and Mn^{3+}, Mn^{3+} and Mn^{VII}, and Cu^+ and Cu^{2+}. Treatment of a mixture of CuCl and 8-hydroxyquinoline with pyridine yields a readily oxidisable substance, the analysis of which corresponds with the formula—

$$(CuC_9H_6ON.C_9H_7ON)_2.C_5H_5N.$$

W. C. JOHNSON

3962. **Polarographic reduction of the permanganate ion on platinum and mercury electrodes.** O. A. Songina and Z. B. Rozhdestvenskaya (Kazakh State Univ., Alma-Ata). *Zhur. Anal. Khim.*, 1956, **11** (6), 717–722.—At the rotating platinum electrode the height of the wave due to reduction of MnO_4^- is proportional to concn., but it is less on an electrode that has been polarised previously at negative potentials because of interaction between MnO_4^- and H adsorbed on the platinum. On the dropping mercury electrode the wave height is proportional to MnO_4^- concn., but depends on the H_2SO_4 concn. This wave appears to be due to reduction of Hg ions which have been formed by oxidation of Hg by MnO_4^-. It can be used for determining the concn. of MnO_4^-. G. S. SMITH

3963. **Use of cacotheline as an oxidation - reduction indicator before the volumetric oxidation of iron.** D. N. Hume and I. M. Kolthoff (Univ. Minnesota, Minneapolis, U.S.A.). *Anal. Chim. Acta*, 1957, **16** (5), 415–418.—After the reduction of Fe^{3+} with *N* $SnCl_2$, according to the classical method, the excess of $SnCl_2$ is oxidised by titrating the hot soln. rapidly with 0·02 to 0·03 *N* $Ce(SO_4)_2$. Cacotheline is used as indicator (3 drops of a 1% suspension in H_2O), the colour changing from violet through brown to yellow. The soln. is then diluted and acidified with H_2SO_4 and the Fe^{2+} are titrated with 0·1 *N* $Ce(SO_4)_2$, 1:10-phenanthroline - ferrous complex being used as indicator. Other standard methods may also be used for the final titration.

W. C. JOHNSON

3964. **Induced reactions in cerimetry. II. With iron (II) as inductor.** G. Gopala Rao, P. Jagan Mohan and M. N. Sastri (Andhra Univ., Waltair, India). *Z. anal. Chem.*, 1957, **156** (5), 336–339 (in English).—It has been found that the oxidation of Fe^{2+} by $Ce(SO_4)_2$ induces the oxidation of oxalic acid. Oxalic acid thus interferes in the cerimetric determination of Fe^{2+}. The induction is suppressed, but not completely, by H_3PO_4. G. BURGER

3965. **Polarographic determination of iron in solutions containing lead.** S. G. Koltȳpin. Report of symposium: Sovrem. Metodȳ Anal. Metall. M., Metallurgizdat, 1955, 128–132; *Ref. Zhur., Khim.*, 1956, Abstr. No. 22,724.—Ions of Pb^{II} cause a considerable lowering of the diffusion current of Fe^{III}, which is reduced at a more positive potential than Pb^{II}. The latter most strongly (by 8 to 30%) reduces the value of the diffusion current of Fe^{III} at low concn. (2×10^{-4} to 10^{-3} mole per litre of Fe), less noticeably (by 4 to 8%) at higher concn. (10^{-3} to 2×10^{-3} mole per litre of Fe). These errors may be allowed for by making corrections from an experimentally obtained curve showing the decrease in the diffusion current of Fe^{III} in the presence of Pb^{II}. C. D. KOPKIN

3966. **Tannic acid in analytical chemistry. Ultraviolet absorption of tannic acid and photometric determination of iron and titanium.** Chozo Yoshimura and Kisaburo Oue (Fac. of Engng, Kinki Univ., Fuse, Osaka). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1957, **78** (3), 320–323.—The characteristic absorption of tannic acid (**I**) at 280 mμ obeys Beer's law for < 30 μg per ml. During autoxidation, this extinction decreases and another peak appears at 250 mμ, presumably due to an oxidation product, as the same peak also appears on oxidation with ceric sulphate. This can be satisfactorily used instead of the conventional $KMnO_4$ for the volumetric determination of **I**. The sample is made 4 *N* in H_2SO_4, treated with a known amount of $Ce(SO_4)_2$ on a water bath and the excess is titrated with Fe^{2+} soln., with *o*-phenanthroline as indicator. The reaction of **I** with Fe^{3+} proceeds quant. at pH 4·5 to 6·0 in an acetate buffer; the excess of **I** is extractable with butanol. The extinction of the remaining Fe - **I** complex is proportional to the concn. of Fe for < 4 μg per ml at 550 mμ. The Ti - **I** complex is also extracted under the given conditions without affecting the extinction of the aq. layer; Fe in titanium can thus be easily determined. K. SAITO

3967. **Determination of iron oxide in chrome ores.** N. Skalla and K. Reischl. *Radex Rdsch.*, 1956, (6), 294–299.—After a critical survey of methods of determining the iron oxide content of chrome ore, the methods of sulphuric acid solution in a bomb tube and phosphoric acid - vanadium pentoxide solution are described. The former method, when carried out at 250° with CO_2 as protective gas, is more accurate, but the latter method is quicker and more suitable for routine production control. J. IRON ST. INST. ABSTR.

3968. **Conductimetric estimation of ferrocyanides by titration with potassium dichromate.** D. Ceauşescu and F. Ciolan. *Stud. Cercet. Chim., Cluj*, 1956, **7** (1–4), 77–80.—The reaction represented by the equation—

$$K_2Cr_2O_7 + 6K_4Fe(CN)_6 + 14HCl = 6K_3Fe(CN)_6 + 2CrCl_3 + 8KCl + 7H_2O,$$

can be followed volumetrically, with benzidine as redox indicator or by conductimetric titration. H. SHER

3969. **Use of certain colourless organic compounds for the detection of the ferricyanide ion.** E. A. Pozigun. *Trudȳ Odessk. Univ., Ser. Khim. Nauk*, 1956, **146** (5), 75–76; *Ref. Zhur., Khim.*, 1957, Abstr. No. 23,495.—The conditions are studied for the detection of $[Fe(CN)_6]^{3-}$ by the formation of coloured compounds with 1- and 2-naphthylamine (**I** and **II**), 1- and 2-naphthol (**III** and **IV**), catechol (**V**) and quinol (**VI**), and also the influence of a series of cations and anions on the indicated reactions. The limits of detection in μg for **I**, **II**, **III**, **IV**, **V** and **VI**, respectively, are 2, 2, 6·6, 8, 2 and 20, at limiting dilutions of 1 in 1×10^4, 1×10^4, 3×10^3, $2{\cdot}5 \times 10^3$, 1×10^4 and 1×10^5. C. D. KOPKIN

3970. **Direct-reading spectrometric analysis of alloy cast-iron.** R. Bartel and A. Goldblatt (Spectro Service Lab., Chicago, Ill., U.S.A.). *Spectrochim. Acta*, 1957, **9** (3), 227–234.—Excitation conditions have been established which eliminate the metallurgical effects of carbon in the spectrographic analysis of iron and steel by the point-to-plane technique. As a result, iron and steel standards can be used interchangeably to prepare analytical curves for alloy cast-iron. K. A. PROCTOR

3971. **Photometric procedure for the examination of cast iron and steel.** H. Kopp and E. Zindel. *Giesserei*, 1956, **43**, 210–216.—Combined analysis of Si, P, Mn, Cr, Mo, Ni and Ti with the perchloric acid process and of W, Mo, V, Co, Cr, Ni, Mn and Ti by using a single stock soln. is described. The Leifo photometer and Zeiss electrophotometric apparatus are used. CHEM. ABSTR.

3972. **Chlorine method for the determination of non-metallic inclusions in steel.** C. W. Short, R. S. Roberts and G. Croall (John Lysaght's Scunthorpe Works, Ltd.). *J. Iron St. Inst.*, 1957, **186** (1), 85–89.—Chlorination of steel samples in a furnace at 350°, the $FeCl_3$ being volatilised and the residue being dissolved and analysed, is the basis of the method described. A detailed comparison of results (total O) obtained by this method and by the vacuum-fusion method is tabulated. S.C.I. ABSTR.

3973. **The high sensitivity determination of carbon [in iron and steel] with a recording conductivity apparatus.** W. Koch and H. Malissa (Max Planck Inst. f. Eisenforsch., Düsseldorf). *Arch. Eisenhüttenw.*, 1956, **27** (11), 695–699.—The gas-analysis apparatus of Schmidt and Baasch has been adapted for the estimation of small amounts of CO_2 from the combustion of iron and steel. The CO_2 is absorbed in NaOH soln. and the changes in conductivity are automatically recorded. Changes in the rate of combustion can be followed and blank values are very small. The deviation is well within the limits set by the Chemists Committee of the German Iron Metallurgists Association. F. J. M.

3974. **Wet chemical nitrogen analysis in steel.** J. Calmettes and J. Drain. *Rev. Métall.*, 1956, **53**, 682–688.—Nitrogen is determined by distillation of NH_3 from the soln. of the steel into a mixture of

NaOCl and Na phenoxide to form a blue indophenoxide. The absorption of the blue soln. is measured. CHEM. ABSTR.

3975. **Determination of nitrogen in cast iron.** J. Marot. *Rev. Metall.*, 1956, **53**, 689–700.—An apparatus for the vacuum fusion of iron in the presence of Na_2O_2 was developed. Discrepancies found are the result of escaping gaseous N or transformation of the N in non-distillable compounds or compounds that cannot be titrated by acidimetric methods. A heat-treatment of the sample at 950° for 3 hr. increases the accuracy of the determination. CHEM. ABSTR.

3976. **Colorimetric determination of phosphorus in steel and copper-base alloys.** W. T. Elwell and H. N. Wilson (I.C.I. Ltd., Kynoch Works, Witton, Birmingham, England). *Analyst*, 1957, **82**, 453–454.—In the method previously described (*Anal. Abstr.*, 1956, **3**, 2739), interference by As is said to account for a positive error equiv. to about 1% of its wt. of P. Further experience has shown that the influence of As was under-estimated and, although its presence can still be ignored for most practical purposes, significant error might be introduced with steels of the silicon-transformer type and those containing, say, less than 0·01% of P when the As content exceeds 0·1%. The As may be removed by a simple modification. After solution of the sample in the HCl - HNO_3 mixture, the soln. is evaporated to dryness, cooled, treated with 5 ml of conc. HCl and 5 ml of HBr (sp. gr. 1·46 to 1·49) and warmed to dissolve the residue. The soln. is then evaporated to dryness and cooled, $HClO_4$ (5 ml) is added, and the original procedure is then followed. A. O. JONES

3977. **Determination of zirconium in steel. Direct spectrophotometric method.** R. B. Hahn and J. L. Johnson (Chem. Dept., Wayne State Univ., Detroit, Mich., U.S.A.). *Anal. Chem.*, 1957, **29** (6), 902–903.—The steel is dissolved in HCl and the soln. is evaporated to fumes with $HClO_4$. After dilution, the soln. or an aliquot is electrolysed at the mercury cathode and, after removal of interferences, the soln. is treated with $HClO_4$ and chloranilic acid, and made up to standard vol. The absorption is measured at 525 mμ or at 330 mμ. The concn. of Zr is derived from calibration curves, which are not linear, especially at high concn. Results are said to compare favourably with those of standard methods, and comparison data are given.
D. A. PANTONY

3978. **Photometric determination of silicon and phosphorus in iron and steel.** J. Scheunemann and B. Strieter. *Chem. Tech., Berlin*, 1957, **9** (2), 93–96.—Silicon and P are determined as the molybdic acid and vanadate - molybdic acid complexes, respectively, by colorimetric estimation of soln. in HNO_3 or HNO_3 - HCl. To obtain accurate results it is essential to separate alloyed products (chromium or manganese steel) from unalloyed ones and to adjust the method of analysis accordingly (use of correct acid). Results compare well with those obtained by gravimetric analysis and there is a 60% saving in time and 80% in Mo. The reaction times with ammonium molybdate, the acid concn. and the quality of NaF, for Si, are critical. The method is recommended for the control of steel foundry work and is also applicable to grey cast-iron. C. A. CURTIS

3979. **Bismuthate method of determining chromium in steel not containing vanadium.** P. F. Agafonov (Metallurg. Works, Zlatoust). *Zhur. Anal. Khim.*, 1956, **11** (6), 752–753.—For complete oxidation of Cr by bismuthate in a boiling soln. containing 10 to 25 ml of conc. H_2SO_4 per 100 ml of soln., 1·5 to 2 g is required for 1 g of steel containing up to 3% of Cr, and for a sample wt. of 0·2 g of steel, 2 to 2·5 g is required for 3 to 8% of Cr, 2·5 to 3 g for 8 to 25% of Cr, and 3 to 3·5 g for 25 to 45% of Cr. The excess of bismuthate is removed by addition of KCl or NaCl. With high-chromium steel, the sample (0·2 to 0·5 g) is dissolved in HCl - HNO_3 mixture and the soln. is evaporated to fuming with 15 ml of conc. H_2SO_4. The residue is dissolved in 100 ml of water and the soln. is boiled with a suitable amount of sodium bismuthate for 2 min. After addition of 50 ml of hot water and 15 to 20 ml of 20% KCl or 15% NaCl soln., the soln. is boiled for 2 min., then cooled and mixed with 5 ml of conc. H_3PO_4 and titrated with 0·06 *N* Fe^{2+}, with phenylanthranilic acid as indicator.
G. S. SMITH

3980. **Potentiometric determination of tungsten in steel.** R. Suárez Acosta. *Inst. Hierro y Acero*, 1956, **9**, 586–595.—Dissolve 1 to 5 g of steel in a hot acid mixture (5 ml of 7·5 *N* H_2SO_4 and 20 ml of syrupy H_3PO_4). To dissolve any remaining carbides add 2 ml of conc. HNO_3. Filter and dilute to 100 ml. To a vol. (≡ 15 to 20 mg of W) add 3 times the vol. of 12 *N* HCl and 5 g of pure zinc. After bubbling stops, filter into the reaction cell of the instrument. Connect the potentiometer electrodes and flush the soln. with O-free N. After 15 min. measure the e.m.f. and slowly add 0·1% $CrSO_4$ soln. until a potential of − 400 mV is reached, then make the determination by adding $K_2Cr_2O_7$. The difference in vol. between two potential kinks corresponds to the W content. If three occur, the first corresponds to any Mo present.
CHEM. ABSTR.

3981. **New colour reaction for bivalent cobalt.** G. D. Nessonova and E. K. Pogosyants (Moscow Textile Inst.). *Zhur. Anal. Khim.*, 1956, **11** (6), 754.—Addition of glycerol followed by conc. NaOH to soln. of Co^{2+} gives an intense bluish-violet colour which can be used for detecting Co at a limiting dilution of 1 in $2·5 \times 10^4$. The colour is stable to heating and light, but long contact with the air gives a green colour due to oxidation of Co^{2+}.
G. S. SMITH

3982. **Colour reactions for the detection of cobalt and bismuth.** R. B. Golubstova (A. A. Baĭkov Inst. of Metallurgy, Acad. Sci., USSR). *Zhur. Anal. Khim.*, 1956, **11** (6), 694–697.—By means of 5:6-benzoquinoline in the presence of NH_4SCN, 0·55 μg of Co at a limiting dilution of 1 in $18·2 \times 10^4$ and 4 μg of Bi at a limiting dilution of 1 in 1×10^5 can be detected from the formation of blue and yellow ppt., respectively. G. S. SMITH

3983. **Precipitation paper-chromatography of cations with 8-hydroxyquinoline. III. Some technical improvements for the separation of cobalt, nickel and ferric iron.** Hideo Nagai (Fac. Sci., Kumamoto Univ., Kumamoto). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1956, **77** (12), 1794–1797.—The separation of these ions on a circular filter-paper impregnated with 8-hydroxyquinoline, with 2% acetic acid saturated with *n*-butanol (*Anal. Abstr.*, 1956, **3**, 2399; 1957, **4**, 1425), has

been modified. The uniformity of the paper is increased by treatment of the paper in an air bath at 140°, and the zones of the ions are clearer when the impregnated paper is treated with *n*-butanol before addition of the sample spot. When the pH value of the developer is lower than the lowest pH value for the formation of the metal oxinate, the oxinates, pptd. on the paper, are re-dissolved and subjected to further development, resulting in better separation of the metal ions concerned. In order to lower the pH value of the developer, the addition of *n*-butyric acid (*n*-butyric acid - 2% acetic acid - *n*-butanol - water) (1:20:4:40) is recommended.

IV. The mechanism of the separation of copper, ferric iron, nickel and cobalt. Hideo Nagai. *Ibid.*, 1957, **78** (2), 285–288.—The mechanism of the separation is discussed on the basis of stability of the oxine complexes and their solubility. The sequence of pptn. of insol. metal complexes on the treated paper is the same as that of their stability constants. The presence of Zn does not cause interference with the chromatographic separation, since its zone appears outside that of Co. These two rings are separated with a pale-grey band of $Fe(OH)_3$.

V. Separation of copper, ferric iron, nickel, cobalt, zinc, lead, cadmium, manganese, calcium and magnesium. Hideo Nagai. *Ibid.*, 1957, **78** (6), 840–843.—The separation of cations that form less stable oxinates than that of Zn was studied on the same paper. The ions of Cu, Fe^{III}, Ni, Co, Cd (or Zn or Pb), Mn and Mg (or Ca) were satisfactorily separated, their zones appearing in the given sequence from the centre. Attempts to separate Cd, Pb and Zn, and Ca and Mg on this paper were unsuccessful. Illumination with u.v. light makes for easier observation of the zones. K. SAITO

3984. **Determination of cobalt in cobalt - platinum alloys.** D. H. Wilkins and L. E. Hibbs (General Electric Co., Schenectady, N.Y., U.S.A.). *Anal. Chim. Acta*, 1957, **16** (5), 449–451.—*Procedure* (*i*)—Dissolve a sample, containing 25 to 100 μg of Co, in aqua regia, evaporate to dryness on a steam bath and dissolve the residue in 9 *N* HCl. Transfer the soln. to a column, 1 cm in diameter, containing 10 g of Dowex 1 × 4, 50 to 100 mesh (Cl^- form). Elute the Co with 3 *N* HCl, add to the eluate 6 ml of dil. H_2SO_4 (1:1) and evaporate to fumes. To the residue add 100 ml of water, neutralise with aq. NH_3, add 20 ml of conc. aq. NH_3 in excess and 2 g of $Na_2SO_3.7H_2O$ and dilute to 300 ml. Electrolyse at 70° to 90° with platinum electrodes at a controlled potential of 0·80 V *vs.* the S.C.E. After 15 min. increase to 0·85 V. The deposition of Co is complete in 25 to 30 min. The $PtCl_6^{2-}$ cannot be eluted from the column. *Procedure* (*ii*)—To the soln. of the sample in aqua regia add 6 ml of dil. H_2SO_4 (1:1) and evaporate to fumes. Dissolve the residue in 100 ml of water, add 2 g of hydrazine sulphate and heat at the b.p. for 1 hr. Cool, filter through paper, wash with water, ignite and weigh the Pt. Determine Co in the filtrate as in procedure (*i*). The max. error recorded is 0·4% on a content of Co of 11·4% [procedure (*i*)]. W. C. JOHNSON

3985. **Polarographic determination of palladium on solid electrodes.** M. B. Bardin and Yu. S. Lyalikov (Kishinev State Univ.). *Zhur. Anal. Khim.*, 1956, **11** (6), 704–709.—On stationary or rotating platinum or palladised electrodes, Pd in 0·1 *M* $NaNO_3$ gives a clearly defined polarographic wave with a reduction potential corresponding to 0·6 to 0·7 V applied e.m.f. G. S. SMITH

3986. **Fluorescent X-ray spectroscopic estimations of palladium, platinum, rhodium and iridium.** W. M. MacNevin and E. A. Hakkila (Ohio State Univ., Columbus, U.S.A.). *Anal. Chem.*, 1957, **29** (7), 1019–1022.—The four elements can be rapidly determined in soln. by X-ray fluorescence with sensitivities of detection of 0·10, 0·20, 0·14 and 0·02 mg per ml, respectively, for Pt, Pd, Rh and Ir. The sample soln. is dried on heavy absorbent paper, which is placed in the sample holder of the instrument. Evaporation errors and soln. expansion errors encountered with liquid samples are thus eliminated. The accuracy is controlled by the effects of mutual enhancement, absorption and line-proximity, and the percentage errors, calculated on an average error in counting for one standard deviation of 1·86%, were 12·6% for Pt, 6·9% for Pd, 13·0% for Rh and 7·0% for Ir.
K. A. PROCTOR

3987. **Comparative study of different methods of determining exchangeable cations from clays and micas.** S. P. Mitra and Dharam Prakash (Sheila Dhar Inst. of Soil Sci., Univ. of Allahabad, India). *Anal. Chim. Acta*, 1957, **16** (5), 431–435.—Various minerals are used in a comparison of published methods for the determination of exchangeable ions. It is concluded that Schollenberger's method (*Brit. Abstr. B*, 1927, 886) of leaching with neutral *N* ammonium acetate is the most satisfactory.
W. C. JOHNSON

3988. **Quantitative spectrochemical analyses of some silicate and carbonate rocks and iron ores with the Stallwood air-jet.** J. E. Hawley and Graham MacDonald (Miller Research Lab., Queen's Univ., Kingston, Ontario). *Geochim. et Cosmoch. Acta*, 1956, **10**, 197–223.—In this d.c. arc method, $SrCO_3$ is used as internal standard and the air-jet described in detail by Stallwood (*cf. Anal. Abstr.*, 1954, **1**, 1736) is employed to yield an even upward current of air on all sides of the sample electrode. Air is supplied from a tank fed by pump, and air-pressure is held at 9 in. of mercury, which prevents flaring out of the arc flame, yields sharper lines and reduces CN band-spectra, and gives films with almost no background. Other advantages are the elimination of selective volatilisation, interference, and other variable matrix effects on the sensitivity; a great improvement in linearity is obtained in the intensity - concentration curves. Samples are mixed with $SrCO_3$ and buffer graphite in the ratio 1:1:2 for major, minor and trace elements in most rocks, but $BaCO_3$ is more suitable for basic silicate rocks and for Mg in carbonates, while for determinations of Ba, Sr and Pb in siliceous igneous or metamorphic rocks K_2SO_4 is used. For siliceous granitic rocks an accuracy of 5% or less is indicated for the major constituents, and an acceptable accuracy for minor constituents is shown. Full details of line pairs used are given. R. A. HOWIE

See also Abstract 4204.

3.—ORGANIC ANALYSIS

3989. **Interaction of β-particles with organic compounds.** D. C. Müller (Los Alamos Sci. Lab., N.M., U.S.A.). *Anal. Chem.*, 1957, **29** (6), 975–978.—General principles which govern the back-scattering of β-particles from matter are applied to

representative organic compounds. The anomaly of H which exhibits negative scattering is resolved, and a reliable value deduced for it. It is shown that the back-scattering of compounds is accurately predictable from the intrinsic scattering of constituent atoms. K. A. PROCTOR

3990. **Apparatus for wet-oxidation of organic samples and carbon dioxide trapping for subsequent radioactive assay.** J. L. Rabinowitz (Veterans Admin. Hosp. Radioisotope Service, Philadelphia, Pa., U.S.A.). *Anal. Chem.*, 1957, **29** (6), 982–984.—An all-glass apparatus is described. The sample is oxidised at 160° to 170° (Wood's-metal bath) for 2 hr. and the gas evolved is carried, by N or He, through 5% $KMnO_4$ in 0·5 *N* H_2SO_4 into saturated $Ba(OH)_2$ soln. layered with toluene. The reaction vessel and both absorption vessels are centrifuge tubes fitted with standard taper joints, and provision is made for addition of the oxidising mixture from a separating funnel and for addition of a catalyst through a side-arm. Sublimed, partially oxidised material is trapped on a solid CO_2 finger and can be transferred back into the reaction-vessel for "recycling". The $BaCO_3$ is washed and dried in the centrifuge tube, and weighed before conversion into a form suitable for radioactive assay. If desired, the tube containing the $BaCO_3$ can be substituted for the reaction vessel, and the CO_2 liberated and re-absorbed. Figures are quoted for several substances which show the improvement in recovery brought about by "recycling", in both gravimetric and radioactive assays. The apparatus can be adapted to a gaseous assay system, and can be used for other analyses involving the liberation and trapping of CO_2. R. E. ESSERY

3991. **Simultaneous determination of carbon, hydrogen and sulphur in organic materials.** N. V. Sokolova (Inst. of High Molecular Compounds, Acad. Sci., USSR). *Zhur. Anal. Khim.*, 1956, **11** (6), 728–730.—With the method of Korshun *et al.* (*Brit. Abstr. C*, 1952, 520) the active life of the Ag used for absorbing compounds of S is very short. The use of silvered pumice is recommended.
G. S. SMITH

3992. **Simultaneous determination of oxygen and halogens (chlorine, bromine and iodine) in organic compounds.** M. O. Korshun and E. A. Bondarevskaya (Inst. Hetero-org. Compds., Acad. Sci. USSR, Moscow). *Dokl. Akad. Nauk SSSR*, 1956, **110** (2), 220–222.—The method is based on the probability of evolution of halogens as hydrogen halides during the decomposition of the sample, in contact with H. The sample is decomposed in a quartz test-tube and the decomposition products are deposited on the catalyst (platinised soot heated to 900° and formed in a plug 3 cm long), where they react in a stream of N and pass into an absorption train of Ascarite and anhydrone, where hydrogen halide (HX) is absorbed. The CO passes into a tube containing CuO heated to 100°, where it is oxidised to CO_2, which is absorbed as described above. Since the formation of HX occurs at the expense of H generated in the decomposition, difficulties are encountered if the sample contains little or no H. Also, much HX is retained by the catalyst and is only slowly removed by N. The samples were therefore mixed with standard hydrocarbons, *e.g.*, paraffin, to supply the needed H, and a subsequent passage of N readily removed the adsorbed HX. Several halogen- and O-containing substances were analysed with an error $\not> 0{\cdot}2\%$. CHEM. ABSTR.

3993. **A method for the determination of the oxygen-18 concentration of the oxygen of organic compounds.** D. Rittenberg and L. Ponticorvo (Columbia Univ., Mo., U.S.A.). *Intern. J. Appl. Radiation and Isotopes*, 1956, **1**, 208–214.—Oxygen-containing organic compounds are oxidised to CO_2 of the same isotopic oxygen concn. as the original compound by $HgCl_2$ (or Cu_2Cl_2 or Cl) at 350° to 530° in sealed Pyrex-glass tubes, from which the CO_2 can be collected and measured by mass spectrograph. The HCl developed is removed by quinoline. The following compounds are tested (^{18}O in atom % excess by $HgCl_2$ method and by independent method given)—glucose-1-^{18}O, 1·05, 1·06; tyrosine-COOH-^{18}O, 4·23, 4·32; α-amino-γ-phenylbutyric acid-^{18}O, 1·28, 1·33; phenylalanine-^{18}O, 1·28, 1·29; N-dinitrophenylalanine-^{18}O, 0·43, 0·40; arginine-^{18}O, 0·96, 1·00; benzamide-^{18}O, 0·71, 0·72. As a further test the mixture of 14·5 mg of glycine-^{18}O (0·98 atom % excess by the $HgCl_2$ method) and 45·2 mg of ordinary α(N)-benzoyl-ε(N)-benzylidenelysine amide was analysed—calculated concn. of ^{18}O, 0·579, found, 0·569 atom % excess.
CHEM. ABSTR.

3994. **Dumas micro-determination of nitrogen.** W. J. Kirsten (Inst. of Medical Chem., Univ. of Uppsala, Sweden). *Anal. Chem.*, 1957, **29** (7), 1084–1089.—A rapid, highly accurate method, based on pyrolysis in CO_2 and subsequent combustion over nickel oxide (*cf.* Kirsten and Grunbaum, *Anal. Abstr.*, 1956, **3**, 1038), has been modified to render it suitable for the micro scale. As finally adopted it employs a back-sweeping procedure, a temporary filling contained in a platinum-gauze capsule, a leak arrangement with quartz rod for introduction of the sample, which remains in the tube during combustion, and the use of a pressure slightly above atmospheric in the nitrometer, with an ungreased nitrometer head. By using a fast-weighing single-pan balance, it is claimed that in continuous work a single analysis, from weighing out to calculation of result, takes 15 min. Combustion tubes of opaque quartz were found to be less susceptible to fracture than those of clear quartz. The apparatus is fully described and illustrated. Replicate analyses of five compounds with nitrogen contents ranging from 4·12 to 36·81% gave satisfactory recoveries, the standard deviation being 0·037%. Aq. soln. of organic compounds were evaporated in platinum boats at the back end of the tube during back-sweeping, before combustion in the usual way. Results were then slightly low, but those for serum were better than with micro-Kjeldahl methods. R. E. ESSERY

3995. **Infra-red absorption spectra of methylenedioxy and aryl ether groups.** L. H. Briggs, L. D. Colebrook, H. M. Fales and W. C. Wildman (Univ. Coll., Auckland, N.Z.). *Anal. Chem.*, 1957, **29** (6), 904–911.—A detailed examination has been made of the i.r. spectra of 100 compounds containing methylenedioxy, methoxy and ethoxy groups, and the analytical value of the bands for the detection of the groups is discussed. K. A. PROCTOR

3996. **Determination of mercapto and disulphide groups by specific proton displacement.** R. Benesch and R. E. Benesch (Marine Biol. Lab., Woods Hole, Mass., U.S.A.). *Biochim. Biophys. Acta*, 1957, **23**

(3), 643–644.—The method is based on the reaction of mercapto compounds with iodoacetamide at pH 9 and titration of the acidity produced. *Procedure*—To 1 or 2 ml of test solution containing 0·02 milli-equiv. of thiol add one drop each of phenolphthalein and methyl red indicators. Adjust to the methyl red end-point (pH 5·5), add 0·2 ml of 2 *M* recryst. iodoacetamide and titrate from a microburette with NaOH to phenolphthalein (pH 9). Allow to stand for 2 min. and titrate back to methyl red with acid. Calculate the difference in the two titrations as the mercapto compound under test. Disulphides may be determined similarly after electrolytic reduction to thiols. The method is unsuitable for highly buffered samples.

W. H. C. SHAW

3997. **Determination of boron in some organoboron compounds.** A. J. Krol and K. E. Weber (Callery Chem. Co., Penna, U.S.A.). *U.S. Atomic Energy Comm.*, Rep. CCC–1024–TR–205, 1956, 16 pp. —A procedure was developed for accurate and rapid determination of B in methanol-sol. alkyl hydroxyboranes. The B–C bond is oxidised by H_2O_2 and the B is distilled as methyl borate. The method is also applicable to alkylboranes, decaborane and other methanol-sol. organoboron compounds.

NUCLEAR SCI. ABSTR.

3998. **Detection of iodine-containing compounds on paper chromatograms.** A. M. Gawienowski (Biochem. Inst., Univ. of Texas, Austin, U.S.A.). *Analyst*, 1957, **82**, 452–453.—In the paper-chromatographic method of Bowden *et al.* (*Anal. Abstr.*, 1955, **2**, 735) with ceric sulphate - arsenous acid, the iodine-containing substances appear as white spots on a yellow ground and the colour is stable for one or two days. The life of the chromatograms can be extended to at least a month by spraying them with aq. brucine sulphate soln. The background then becomes crimson and the iodine-containing areas remain white and the contrast is thus increased. Alternatively, 1% aq. sulphanilic acid soln. may be used, producing white spots on a brown background. A. O. JONES

3999. **Method for the controlled burning of combustible materials and analyses of the combustion gases.** A. Schriesheim (Esso Res. & Engng Co., Linden, N.J., U.S.A.). *J. Res. Nat. Bur. Stand.*, 1956, **57** (4), 245–249.—A known quantity of combustible material is burned in a fixed volume of air at a predetermined temperature and the combustion gases are analysed by the mass spectrometer. Hydrogen chloride, if present, is determined in a water wash of the combustion chamber by $AgNO_3$ titration, and CO in concn. below 0·1% by aspiration through an indicator. Several different organic coatings burned at 250°, 400° and 550° showed a progressive increase in the variety of combustion products. J. O. LAY

4000. **Determination of oxetanes [β-epoxides].** R. T. Keen (Res. Center, Hercules Powder Co., Wilmington, Del., U.S.A.). *Anal. Chem.*, 1957, **29** (7), 1041–1044.—The oxetane is converted into a 1:3-chlorohydrin by being heated with a measured excess of pyridinium chloride in anhydrous pyridine, and the excess is back-titrated with standard aq. alkali. The reagent (prep. described) should be about 0·20 *N* in pyridinium chloride, and contain < 0·01% of H_2O. For the estimation, an amount of sample containing 1 to 2 milli-equiv. of oxetane is treated with 25 ml of reagent and refluxed for 3 hr., the condenser being fitted with a $CaCl_2$ guard tube. The titration is then carried out with 0·15 *N* NaOH to phenolphthalein. A rapid method taking 1 hr. involves heating the quantities suggested above under N in a sealed tube at 170° for 30 min.; a heating assembly is described which minimises risk to the operator. (This method may not be applicable to derivatives that undergo side-reactions at high temp.) Results for 9 oxetane derivatives of high purity showed recoveries from 97·3 to 103·0%. Phenols and alcohols interfere slightly, most oxiranes (α-epoxides) interfere quantitatively.

R. E. ESSERY

4001. **Photocolorimetric micro-method of determining lactose and sucrose when present together.** M. N. Tul'chinskiĭ (Leningrad Technol. Inst. of the Refrigeration Industry). *Zhur. Anal. Khim.*, 1956, **11** (6), 742–745.—The method is based on the reduction of K_2CrO_4 by lactose and hydrolysates of sucrose in the presence of Na_2CO_3 and glycerol. The extinction of the soln. is measured on a photocolorimeter with a yellow filter. Sucrose is determined by the use of two calibration curves referring to two known concn. of lactose on which the relation between extinction and sucrose (hydrolysate) content is shown. G. S. SMITH

4002. **Determination of sorbitol.** L. H. Adcock (Howards of Ilford Ltd., Essex, England). *Analyst*, 1957, **82**, 427–434.—Carbohydrates and the intramolecular ethers (monoanhydrides) of sorbitol, often present in association with sorbitol, interfere with its determination by oxidation with periodate. In the method described, sorbitol is separated from carbohydrates by heating the sample under reflux with alkali and removal of the complex mixture of acids derived from the carbohydrate (lactic, saccharinic, etc.) by means of an ion-exchange column. Sorbitol is separated from its anhydrides by paper chromatography. The separated sorbitol may be determined by oxidation in acid soln. at room temp. or at 100° with KIO_4, the excess of KIO_4 being determined by addition of KI and titration of the liberated iodine, or by oxidation in alkaline soln. at room temp., and determination of the formaldehyde produced by spectrophotometric measurement of the colour formed with chromotropic acid. Details of these methods are given, and examples of their application to foods, technical products and biological materials. A. O. JONES

4003. **Mass-spectrometric analysis. Aliphatic aldehydes.** J. A. Gilpin and F. W. McLafferty (Dow Chemical Co., Midland, Mich., U.S.A.). *Anal. Chem.*, 1957, **29** (7), 990–994.—An examination of the mass spectra of 20 saturated aliphatic aldehydes shows certain typical cleavages and rearrangements. In most cases, major cleavage occurs at the bond beta to the aldehyde group, accompanied by rearrangement of one hydrogen to the oxygen-containing fragment. The cleavage is increased by chain-branching adjacent to the beta bond. K. A. PROCTOR

4004. **New colour reaction of aldehydes.** T. Urbański (Inst. of Org. Chem., Polish Acad. of Sci., Warsaw). *Bull. Acad. Polon. Sci., III*, 1956, **4** (9), 599–600.—*Procedure*—The aldehyde soln. (1 ml) is added to a soln. of H acid [0·7 g in conc. H_2SO_4

(100 ml) and H_2O (33·3 ml)] and the mixture is shaken. If a high concn. of aldehyde is present, a yellow or orange colour develops immediately. In lower concn. it is necessary to warm on a steam bath for a few minutes. The sensitivity of the test is high, formaldehyde being detectable in concn. of 0·01% and furfuraldehyde in concn. of 0·002%.
C. A. SLATER

4005. **Paper ionophoresis of aldehydes and ketones in the presence of hydrogen sulphite.** O. Theander (Org.-kem. Inst., Kungl. Sweden). *Acta Chem. Scand.*, 1957, **11** (4), 717–723.—A review of investigations on the paper electrophoresis of aldehyde and keto compounds is given and an account of the behaviour of a wide range of these substances in the presence of a sulphite buffer is described. Tables are included listing the migration of the ions under standard conditions with that of vanillin as a reference. The separation, which depends on the equilibrium in the formation of the sulphite addition complex as well as on the R_F value of the resulting ion, can be used as a means of detection and identification of many carbonyl compounds. Details are provided for preparation of standard buffer soln. The electrophoresis was normally run at room temp. with a potential gradient between 12 and 18·5 V per cm, and the resulting spots were located and identified by use of u.v. light or with soln. of dinitrophenylhydrazine, $AgNO_3$ - Na ethoxide or anisidine hydrochloride as the developing reagents. About 3 to 5 hr. are required for the procedure.
D. G. FORBES

4006. **Differentiating titration of acid mixtures in acetone.** J. S. Fritz and S. S. Yamamura (Inst. for Atomic Research, Iowa State College, Ames, U.S.A.). *Anal. Chem.*, 1957, **29** (7), 1079–1084.—The titration of acid substances (phenols, carboxylic acids, enols, imides and sulphonamides) in acetone has been studied, with 0·1 *N* *n*-butyltriethylammonium hydroxide as titrant and following the titration potentiometrically with a glass electrode and a calomel electrode in which the aq. KCl has been replaced by satd. methanolic KCl. The end-point is obtained from a plot of potential *vs.* vol. of titrant, with 0·4 to 0·8 milli-equiv. of acid in 40 ml of acetone, and adding increments of titrant of such size that a constant change of about 30 mV is obtained. The titrant is standardised potentiometrically against benzoic acid, and a solvent blank is applied. Results show satisfactory recoveries of the compounds examined. It is shown that compounds having different functional acidic groups can be differentiated if there is sufficient difference between the respective acid strengths, which implies that the potential at the start of the inflection of the curve for the stronger acid differs by more than 100 mV from that at the beginning of the curve for the weaker acid. Results for mixtures show percentage recoveries of the individual acids of between 97·8 and 102·8.
R. E. ESSERY

4007. **Separation and identification of saturated and unsaturated fatty acids from formic to dodecanoic acid by gas chromatography.** A. T. James (Nat. Inst. Med. Research, London). *Fette, Seif., Anstrichmitt.*, 1957, **59** (2), 73–77.—Methods for the separation of fatty acids by gas chromatography are discussed and examples of separations achieved are given.
E. HAYES

4008. **Kinetic analysis of mixtures of (±)- and *meso*-dibromosuccinic acids.** L. C. King and M. Fefer (Northwestern Univ., Technol. Inst., Evanston, Ill., U.S.A.). *Anal. Chem.*, 1957, **29** (7), 1056–1058.—The (±)-isomer in acid soln. eliminates HBr at a rate about 10 times as fast as the *meso*-form, both reactions being first-order. After the faster isomer has exhausted itself, the amount of slow component can be obtained by extrapolating the first-order plot back to zero time, and the amount of fast component is obtained by difference. To determine the rate constant, a known weight of acid was dissolved in aq. HCl or HBr, at the operating temp., 70° ± 0·1°, and diluted to 100 ml, these solvents being used to depress self-ionisation and obtain first-order kinetics. At various time-intervals, 10-ml aliquots were titrated with standard alkali, and the rate constant was determined from a plot of $\log(a - x)$ *vs.* t, in the usual way. In mixtures, from the half-life of the fast isomer a time can be calculated after which it is present in negligible amount only, and titration values obtained after this are used for extrapolation to zero time. Figures for rate constants at various temp., and methods for the preparation of kinetically pure specimens of the two isomers, are given, and it is shown that extrapolated plots give reasonably accurate results with known mixtures. The method should be applicable to other dihalosuccinic acids or esters.
R. E. ESSERY

4009. **Infra-red spectra of organic azides.** E. Lieber, C. N. Ramachandra Rao, Tai Siang Chao and C. W. W. Hoffman (De Paul Univ., Chicago, Ill., U.S.A.). *Anal. Chem.*, 1957, **29** (6), 916–918.—The i.r. spectra of ten organic azides were studied to determine the range of frequencies where the strong asymmetric vibration of the azido group was likely to occur. The data showed the N_3 asymmetric vibration to be in the region of 2114 to 2083 cm^{-1}, and confirmed that its constancy was practically independent of the environmental structure.
G. P. COOK

4010. **Sensitive detector crayons for phosgene, hydrogen cyanide, cyanogen chloride and lewisite.** B. Witten and A. Prostak (Army Chem. Center, Md., U.S.A.). *Anal. Chem.*, 1957, **29** (6), 885–887.—Methods of preparation are described for crayons capable of detecting trace concn. of these gases. Cyanogen chloride is detected by a crayon containing a mixture of 4-benzylpyridine and barbituric acid and the white marks from the crayon first turn red and then blue in the presence of this gas. The HCN crayon contains chloramine T and is used in conjunction with the cyanogen chloride crayon to give a red - blue colour in the presence of HCN. The phosgene crayon contains 4-*p*-nitrobenzylpyridine, N-benzylaniline and Na_2CO_3, and changes from pale yellow to red. The lewisite crayon contains 4:4′-bisdimethylaminothiobenzophenone and changes from a pale tan to an intense green - blue.
G. P. COOK

4011. **Volumetric determination of aliphatic and aromatic amines with sodium tetraphenylboron.** A. F. Ievin'sh and É. Yu. Gudrinietse (Latvia State Univ., Riga). *Zhur. Anal. Khim.*, 1956, **11** (6), 735–738.—The soln. (5 to 10 ml) containing the amine (15 to 60 mg) and acidified with HNO_3, H_2SO_4 or acetic acid to pH $\simeq$ 3 is treated with 10 ml of Cl^--free 0·05 *N* Na tetraphenylboron, and diluted to 100 ml. After 10 min. the ppt. is filtered off and

50 ml of the filtrate is treated with a small excess of 0·05 *N* $AgNO_3$ and then diluted to 100 ml. The silver compound is filtered off, and 20 ml of the filtrate is titrated for excess Ag with 0·05 *N* NH_4SCN in the presence of Fe^{3+}. G. S. SMITH

4012. **Determination of aliphatic primary and secondary plus tertiary amines. A modified salicylaldehyde method.** F. E. Critchfield and J. B. Johnson (Carbide and Carbon Chem. Co., S. Charleston, W. Va., U.S.A.). *Anal. Chem.*, 1957, **29** (6), 957–959.—The primary amines are treated with salicylaldehyde in $CHCl_3$ medium and form the salicylaldehyde-imines. The unchanged secondary and tertiary amines are titrated with $HClO_4$ in dioxan, with bromocresol green indicator; the titration is then continued to Congo red indicator and this titre gives a measure of the salicylaldehyde-imine, *i.e.*, the primary amine content. In general the mean deviation for both the primary and secondary amine determinations is ± 0·3%, and fair results can be obtained with amine concn. as low as 1%. G. P. COOK

4013. **Titration of isomeric substituted 5-amino-1:2:3-triazoles in non-aqueous media.** E. Lieber, C. N. Ramachandra Rao and Tai Siang Chao (De Paul Univ., Chicago, Ill., U.S.A.). *Anal. Chem.*, 1957, **29** (6), 932–933.—Non-aqueous titration techniques with isomeric substituted 5-amino-1:2:3-triazoles were compared with the usual aqueous methods. Anhydrous dimethylformamide solvent and Na methoxide titrant, with azo violet as the visual indicator, provided an accurate method for the determination of the acidic isomer. Glacial acetic acid solvent and $HClO_4$ titrant were used for the determination of the basic isomer. Recoveries between 99·99 and 100·05% were obtained from nine substituted 5-amino-1:2:3-triazoles. G. P. COOK

4014. **Determination of monoethanolamine, diethanolamine and triethanolamine in mixtures by partition chromatography.** D. A. Vyakhirev and Yu. N. Suloev (Gorki State Univ.). *Zhur. Anal. Khim.*, 1956, **11** (6), 739–741.—A suspension of 13 g of starch in water-saturated *sec.*-butyl alcohol is poured into a 12-cm-diameter column and the starch is compacted under a pressure of 150 mm of Hg to give a column 150 mm high. The mixture of ethanolamines to be analysed is placed in the column and washed with *sec.*-butyl alcohol at a rate of 0·13 ml per min. The course of the separation of the components is followed by titrations with 0·05 *N* HCl. Under these conditions the optimum amount of each component in the column is ≃ 0·007 g. G. S. SMITH

4015. **Analysis of volatile organic sulphur compounds by gas partition chromatography.** S. A. Ryce and W. A. Bryce (Univ. British Columbia, Vancouver, B.C., Canada). *Anal. Chem.*, 1957, **29** (6), 925–928.—A gas partition chromatographic method for the analysis of a sample containing H_2S, methane-, ethane- and propane-thiols, dimethyl and diethyl sulphides, dimethyl disulphide and thiophen is described. The column comprised a tritolyl phosphate liquid phase on a Celite column, and He was used as the carrier gas. The sulphur compounds were also separated from light hydrocarbons, methanol and ethanol, and mixtures of benzene and thiophen were also resolved. The relationship between retention vol., polarity of the liquid phase and the polarity of the gases being analysed is discussed. G. P. COOK

4016. **New procedure for the estimation of the long-chain alkali alkyl sulphate derivatives of primary alcohols.** J. Renault and J. A. Gautier (Fac. de Pharm., Paris, France). *Bull. Soc. Chim. France*, 1957, (2), 208–211.—The alkyl sulphate derivatives of primary alcohols may be pptd. quant. as their nickel salts in ammoniacal soln., giving complexes of the type $(ROSO_3)_2Ni(NH_3)_4$, if R < $C_{10}H_{21}$. The derivative may be estimated either by a volumetric determination of excess of Ni with EDTA (disodium salt) and murexide, or gravimetrically. *Volumetric procedure*—The alkali alkyl sulphate (0·001 mole) is dissolved in water (25 ml) with warming. The soln. is cooled and $NiCl_2$ (0·2 *M*) (5 ml) and 10 *N* aq. NH_3 (10 ml) are added. The soln. is cooled, transferred to a 50-ml flask and made up to vol. with 10 *N* aq. NH_3. After 10 min. the soln. is filtered and a portion (40 ml) is diluted to 160 ml with water. The Ni is estimated by titration with 0·1 *M* EDTA (disodium salt) in the presence of murexide (0·1 g in 20 ml of water). *Gravimetric procedure*—The complex is pptd. as described above, filtered in a No. 4 sintered glass crucible, washed with a saturated soln. of complex in 10 *N* aq. NH_3, and dried to constant wt. The percentage error is ± 1·92. C. A. SLATER

4017. **Qualitative micro-determination of organic phosphorus compounds.** C. M. Welch and P. W. West (State Univ., Baton Rouge, La., U.S.A.). *Anal. Chem.*, 1957, **29** (6), 874–877.—Three methods are described, two of which involve the use of *o*-dianisidine molybdate reagent and indicate P by the formation of a reddish-brown ppt. The third method is based on the production of molybdenum blue and hydrazine hydrate is used as the reducing agent. The methods are capable of detecting 0·2 μg of combined P and are applicable to acids, esters, acyl halides and anhydrides, together with their thio analogues. Methods are proposed for the degradation of organic compounds of P, and results showed that the general method, involving refluxing with conc. H_2SO_4, was satisfactory. Methods of sampling and the application to air analysis are also discussed. G. P. COOK

4018. **Determination of tributyl phosphate.** R. J. Allen and M. A. DeSesa (National Lead Co. Inc., Winchester, Mass., U.S.A.). *U.S. Atomic Energy Comm.*, Rep. WIN–52, 1956, 27 pp.—Two indirect methods based on the proportional extraction of HNO_3 or U by soln. of tributyl phosphate (**I**) were modified and improved. Also a new, very sensitive, indirect photometric method based on the u.v. absorption of the **I** - uranium complex was developed. NUCLEAR SCI. ABSTR.

4019. **Detection of nerve gases by chemiluminescence.** J. Goldenson (Army Chem. Center, Md., U.S.A.). *Anal. Chem.*, 1957, **29** (6), 877–879.—Nerve gases, which are organic quinquevalent phosphorus compounds having structures either of the type R(R′O)POF or $(R_2N)(R'O)(PO)CN$ with very reactive P–F or P–CN linkages, can be detected by the chemiluminescence produced from a soln. of the gas with 3-aminophthalhydrazide (luminol) and sodium perborate. A plot of max.

luminosity values *vs.* the concn. of nerve gas gave an approximate linear relationship. As little as 0·5 μg of nerve gas can be readily detected.
G. P. Cook

4020. **The separation of naphthalene and its hydrogenated products by vapour-phase chromatography.** R. M. Soemantri and H. I. Waterman (Univ. Chemical Engng, Delft, Holland). *J. Inst. Petrol.*, 1957, **43**, 94–99.—Solid mixtures can be liquefied before the analysis by heating or by adding benzene to them, without disturbing the quant. analysis. Operational variables are discussed, together with the method of calibration and the quant. interpretation of the chromatogram. Only very small samples (0·10 to 0·20 ml) are required and concn. as small as 1% can be detected quant. The accuracy of the method is ± 1·5% absolute.
O. M. Whitton

4021. **The theory and practice of liquid - liquid partition chromatography of phenols.** D. White and G. A. Vaughan (The Coal Tar Res. Ass., Gomersal, Leeds, England). *Anal. Chim. Acta*, 1957, **16** (5), 439–449.—The design of liquid - liquid partition chromatographic columns is determined by an equation that relates the separation factors and column characteristics with the number of theoretical plates required for a given separation. This approach provides methods for the determination of phenol in tar-acid mixtures and for the separation of the three isomeric cresols.
W. C. Johnson

4022. **Estimation of phenols by means of 4-aminophenazone.** R. Drábek (Inst. Wasserwirtschaft, Brno, Czechoslovakia). *Chem. Tech., Berlin*, 1957, **9** (2), 77–81.—When phenolic soln. are treated with 4-aminophenazone in the presence of oxidising agents [$K_3Fe(CN)_6$ or $(NH_4)_2S_2O_8$] at pH 10, with 6 *N* aq. NH_3 as buffer, a red colour is obtained which changes to orange - yellow when extracted with $CHCl_3$, and can then be determined photometrically. The method is accurate and sensitive to 0·02 mg per litre, and is suitable for the determination of phenols in waste waters. Strongly oxidising or reducing agents must be absent, as well as those metal ions and compounds that react with ferricyanide, such as H_2S.
C. A. Curtis

4023. **Rapid quantitative determination of hydroquinone [quinol].** C. B. Jordan (Coating & Chem. Lab., Aberdeen Proving Ground, Md., U.S.A.). *Anal. Chem.*, 1957, **29** (7), 1097–1098.—The pH of the sample is adjusted to between 3·8 and 5·0 with HCl or NaOH, and a 50-ml aliquot is titrated with 4% aq. $FeCl_3.6H_2O$, at a rate of 10 to 20 drops per min., against a yellow background and shaking the flask after addition of each drop. The addition of reagent produces a green colour which immediately disappears, and the end-point is reached when the green colour is no longer formed. The iron soln. is standardised by titration of 50 ml of a 0·2% aq. soln. of pure quinol. Normal results show a max. error of 3·3% of the quinol in samples containing 0·02 to 1·0 g. Compounds that are oxidised by $FeCl_3$, or which contain colours which mask the end-point, interfere.
R. E. Essery

4024. **Separation and identification of acids by paper chromatography. II. Benzoic, *p*-hydroxybenzoic and salicylic acids.** L. C. Mitchell (Div. Food, Food & Drug Admin., Dept. of Health, Education and Welfare, Washington, D.C., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1957, **40** (2), 592–594.—These acids are separated and identified by paper chromatography, with a mixture of acetone (90 ml), aq. NH_3 (3 ml) and water (to 100 ml) as the mobile solvent. The dry papers are sprayed with an ammoniacal soln. of $AgNO_3$ in ethanol and then, after being dried, with a soln. of pyrogallol in ethanol. The sensitivities are about 7, 3 and 3 μg, respectively.
A. A. Eldridge

4025. **2-Naphthyloxyacetic acid. An analytical study. II. Determination by a fluorimetric method.** J. Minczewski (Anal. Dept., Inst. of General Chem., Warsaw). *Chem. Anal., Warsaw*, 1957, **2** (1), 62–68.—The method is suitable for testing aq. soln. and mixtures with talc or bran, but not for soil. *Procedure*—The soln., containing 1 to 10 μg of 2-naphthyloxyacetic acid (**I**), is evaporated to dryness, the residue is treated with 10 drops of the reagent (1% Na_3AsO_4 in conc. H_2SO_4) and heated at 105° to 110° for 10 min. After cooling, the mixture is diluted, treated with 10% aq. NH_3 (5 ml) and the fluorescence is measured with a fluorimeter or estimated visually under a u.v. lamp. The accuracy is within ± 10% (5 to 10 μg of **I** per ml) for fluorimetric determinations or ± 0·5 μg of **I** for visual determinations.

III. Spectrophotometric determination in the ultraviolet. J. Minczewski. *Ibid.*, 1957, **2** (1), 69–76.—An analytical method for **I**, which makes use of the strong absorption of its aq. soln. at 225 mμ, is described. The method is applicable to aq. extracts of soil treated with **I**. The error with straight aq. soln. containing about 5 μg of **I** per ml was ± 1·7%; with light-soil extracts the error was from 1 to 2 μg of **I** per g and from 3 to 5 μg of **I** per g for heavy soils.

IV. Testing of technical 2-naphthyloxyacetic acid and its sodium salt. J. Minczewski. *Ibid.*, 1957, **2** (1), 105–107.—A soln. of technical **I** in 50% aq. ethanol is passed through a column of Wofatit-F ion-exchange resin. The eluate is boiled to remove CO_2 and the acid is determined by titration with standard alkali. Sodium carbonate is estimated indirectly by determining total Na as Na_2SO_4 and correcting for the sodium content of the sodium salt of **I**.
K. F. Sporek

4026. **Technical analysis of dimethylaniline.** M. N. Karpinskiĭ. *Trudy Leningr. Tekhnol. Inst. im. V. M. Molotova*, 1956, (4), 275–278; *Ref. Zhur., Khim.*, 1957, Abstr. No. 23,532.—The method consists in the oxidation of dimethylaniline (**I**) in acid medium and its condensation with phenol to form the dye methyl violet, with comparison of the colour formed against a standard. Mix about 0·05 g of sample with finely ground NaCl, $CuSO_4.5H_2O$ and phenol, maintain at 60° or 65° for 5, 6 or 7 hr., and after adding a few drops of HCl place the mixture on a boiling-water bath for 30 min. Extract the dye formed with ethanol and add to 25 g of kaolin a vol. of the soln. calculated from the formula $T = 1/1{\cdot}084\ W$, where T = volume of dye soln. in ml, and W = wt. of sample of **I**. Compare the colour with a standard soln. of the dye.
C. D. Kopkin

4027. **Paper electrophoresis of aromatic amines, a critical study. *p*-Nitrophenyldiazonium fluoroborate, a new colour reagent for aromatic amines.** C. Hanot (Univ. of Ghent, Belgium). *Bull. Soc. Chim. Belg.*, 1957, **66** (1–2), 76–92 (in English).—The reaction is carried out with a 0·5% aq. soln. of the reagent. Colours developed in neutral and

alkaline soln. range from light yellow through red to violet. The colour reactions of 30 aromatic amines and phenols are listed. Methods of separating aromatic amines by paper electrophoresis have also been worked out, and an investigation of the phenomenon of paper electrophoresis in a closed chamber has been made. A method of working out the mobilities of migrating amines on paper is described, and the system of electrophoresis with continuous evaporation has been studied. It is concluded that a uniform migration of aromatic amines in a closed chamber may be obtained by lowering the ionic strength of the (preferably volatile) electrolyte soln., by uniform wetting of the paper, and by keeping the paper horizontal.

C. A. SLATER

4028. **Near-infra-red analysis of N-alkyl and N-alkyl-N-hydroxyalkyl aromatic amine mixtures.** K. Whetsel, W. E. Roberson and M. W. Krell (Tennessee Eastman Co., Kingsport, Tenn., U.S.A.). *Anal. Chem.*, 1957, **29** (7), 1006–1009.—By using the O–H and N–H overtone bands near 1·4 and 1·5 μ, respectively, N-ethylaniline and N-ethyl-N-2-hydroxyethylaniline can be determined in mixtures covering the entire concn. range. The standard deviation is $\simeq \pm 1\%$ for the determination of both components, and $\pm 0{\cdot}1\%$ for the determination of N-ethylaniline only. There is no interaction between the two compounds, but aniline interferes seriously with the determination of N-ethylaniline. The interference of water is negligible. Similar methods may be used with mixtures of N-ethyl-*m*-toluidine and N-2:3-dihydroxypropyl-N-ethyl-*m*-toluidine.

K. A. PROCTOR

4029. **Titanometric determination of the oxime of *cyclo*hexanone.** J. Proházka, K. Czerepko and J. Jansa (Inst. Tech. Chem., Usti, Czechoslovakia). *Chem. Anal., Warsaw*, 1957, **2** (1), 92–96.—The oxime of *cyclo*hexanone is hydrolysed by dilute H_2SO_4 to hydroxylamine, and this is determined by reduction with $TiCl_3$. *Procedure*—To $\nearrow$ 100 ml of a soln. containing 0·1 to 0·2 g of *cyclo*hexanone oxime add 1 ml of conc. H_2SO_4 and boil for 45 min. Add 10 ml of *N* NH_4SCN, de-oxygenate the soln. by passing CO_2, add an excess of 0·1 *N* $TiCl_3$ and back-titrate with 0·1 *N* ferric alum. The error was $\nearrow \pm 1{\cdot}5\%$.

K. F. SPOREK

4030. **Molecular spectroscopic analysis of unbranched and branched hydrocarbons. III. Intensity of C–H deformation vibrational bands of paraffins.** H. Luther and G. Czerwony. *Z. physik. Chem.*, 1956, **6**, 286–314.—The max. and integral extinction and absorption coeff. of the C–H deformation vibrational bonds of normal paraffins up to C_{32}, of methylnonanes and of some other isoparaffins have been measured between 700 and 800 and between 1300 and 1500 cm^{-1} in different solvents by means of a Perkin-Elmer double-beam spectrometer. The shares of the CH_2 and CH_3 group oscillations of the bands have been determined. The resulting integral extinction coeff. are, in abs. units, for the CH_2 pendulum vibration at 720 cm^{-1}: $0{\cdot}0604 \times 10^{-7}$; for the symmetric CH_3 stretching vibration at 1380 cm^{-1}: $0{\cdot}249 \times 10^{-7}$; for the asymmetric CH_3 stretching vibration at 1450 cm^{-1}: $0{\cdot}217 \times 10^{-7}$ sq. cm per mole sec. The results are discussed with respect to their analytical applications.

CHEM. ABSTR.

4031. **Determination of normal paraffins in olefin-free petroleum distillates by molecular-sieve sorption and refractometry.** R. D. Schwartz and D. J. Brasseaux (Shell Development Co., Houston, Tex., U.S.A.). *Anal. Chem.*, 1957, **29** (7), 1022–1026.—Heptane, octane, nonane and decane can be determined in crude petroleum by first distilling to yield fractions containing only one normal paraffin, fractionating the distillates on a chromatographic column packed with Linde Type 5A Molecular Sieve, and determining the refractive indices of portions of the eluate. The normal paraffin content is calculated from the refractive indices of the distillate and the normal paraffin-free eluate and the known value for the refractive index of the normal paraffin assumed to be present. The results show an average precision of better than 1% and an average error of less than 2% of the normal paraffin content.

K. A. PROCTOR

4032. **The group structure of petroleum fractions. I. Group structure analysis by means of infra-red spectroscopy.** G. Brandes (Zentrallab. Deutsch. Erdöl-A-G., Hamburg-Wilhelmsburg). *Brennst-Chemie*, 1956, **37** (17–18), 263–267.—The relationship between the i.r. absorption properties and the group structure analysis was quickly determined by the *n-d*-M method (van Nes and van Westen, "Aspects of the Constitution of Mineral Oils," Amsterdam/New York, 1951) with excellent reproducibility in (*a*) petroleum fractions of mol. wt. 290 to 500, *i.e.*, gas oils to cylinder oils in concn. C_A 0 to 60% and C_P 40 to 70% when C_A is $> 25\%$, (*b*) mixtures of oils in these concn. ranges when the additives do not absorb at the relevant wavelength, (*c*) the determination of C_A in extracts.

F. J. M.

4033. **Removal of elementary sulphur from hydrocarbon fractions.** M. Blumer (Shell Development Co., Houston, Tex., U.S.A.). *Anal. Chem.*, 1957, **29** (7), 1039–1041.—Elementary S reacts with finely divided copper at room temp. This reaction is used for its removal from hydrocarbon fractions by simple percolation through a column of copper powder (prep. described). The sample, dissolved in *n*-pentane, or benzene if much crystallisable S is present, is run through the column at a rate of 1 to 2 drops per sec., the column is eluted with 40 ml of the same solvent, and the combined eluates are treated for removal of solvent. If stored in ice, the copper powder retains its activity for at least 6 months and a 10-ml bed will retain 200 to 300 mg of S. The column should be repacked when two-thirds of its vol. is converted into black sulphide. The method is not satisfactory for very complex mixtures, and should be used only for fractions obtained by chromatography or distillation, containing saturated and the more simple aromatic hydrocarbons.

R. E. ESSERY

4034. **Potentiometric methods of studying high molecular compounds of petroleum. II. Potentiometric determination of saponification values in solutions of petroleum resins.** S. R. Sergienko, P. N. Galich, N. A. Izmaĭlov and L. L. Spivak (Inst. of Petroleum, Acad. Sci., USSR, Moscow). *Zhur. Anal. Khim.*, 1956, **11** (6), 731–734.—The sample is dissolved in a mixture of ethanol and benzene (2:5), then mixed with a 5 to 10-fold excess of ethanolic 0·1 *N* KOH and heated on a water bath under a reflux condenser for 1 hr.

without admission of CO_2. The hot soln. is titrated potentiometrically with 0·1 *N* HCl in a CO_2-free atmosphere, glass and calomel electrodes being used. G. S. SMITH

4035. **Apparatus for differential thermal analysis of lubricating greases.** D. B. Cox and J. F. McGlynn (Socony Mobil Oil Co., Inc., Brooklyn, N.Y., U.S.A.). *Anal. Chem.*, 1957, **29** (6), 960–963.—The apparatus described operates automatically in controlling heating rates, and records all pertinent temp. and differential temp. Five different determinations can be run simultaneously. Experimental results reported include a re-examination of the phase change behaviour of pure Li stearate, and a new phase diagram for the model grease system Li stearate - *n*-hexadecane. G. P. COOK

4036. **The de-mineralisation of coal for analytical purposes.** W. Radmacher and P. Mohrhauer (Chem. Lab., Ruhrkohlen-Beratung G.m.b.H., Essen). *BrennstChemie*, 1956, **37** (21–22), 353–358.—The presence of large quantities of mineral matter in coal affects not only the ash content but the estimation of other properties by which it is characterised. A simple procedure for its removal is to extract the granulated coal with HCl, wash, and dry under vacuum. The mineral content is thereby reduced to a level at which its influence on other analytical data of the coal is negligible. F. J. M.

4037. **Rapid determination of the water content of coal and coke.** W. Radmacher and P. Mohrhauer. *Glückauf*, 1956, **92**, 166–171.—The principle of the determination is based on a density change of a $ZnCl_2$ - LiCl soln. A calibration curve is prepd. by dissolving 60 g of LiCl in 200 ml of an aq. $ZnCl_2$ soln. (sp. gr. 1·75), and measuring its density after the addition of known amounts of water (at 20°). The addition of 1 g of water to 100 ml of soln. lowers the density 0·0006 unit. The temp. increase of 1° lowers the density 0·0004 unit. Finely granulated coal (200 g if the water content is below 12%, 100 g if above) is added to 200 ml of $ZnCl_2$ - LiCl soln. and shaken, then set aside for 20 min., and filtered through a double fluted filter; the density and temp. are measured, and the water content is calculated, with reference to a calibration curve. Coke samples finely ground (max. grain size 5 mm) and evacuated before extraction with water can be treated by this method. CHEM. ABSTR.

4038. **Volatile matter in coke.** N. N. Das Gupta, V. V. Rao and A. K. Roy Chowdhury. *J. Inst. Chem. India*, 1956, **28**, 118–128.—The effects of various details of experimental procedure on the determination of volatile matter (**I**) in coke were investigated. The large increase in **I** (up to 55%) on storage (*J. Inst. Fuel*, 1954, **27**, 201) is confirmed. It is concluded that a value for **I** slightly in excess of specification should not disqualify coke for use in blast furnaces or for making synthesis gas. A. B. DENSHAM

4039. **Reversed-phase chromatography. I. Identification of fat-soluble dyes.** M. R. Verma and Ramji Dass (Nat. Phys. Lab., New Delhi, India). *J. Sci. Ind. Res., B, India*, 1957, **16** (3), 131–134.—A chromatographic method has been developed on paper prepared by impregnation with liquid paraffin, *n*-dodecanol, oleic acid or diethylene glycol monostearate. The elution is carried out with various mixtures of water, acetone, dioxan, methanol, ethanediol, acetic acid and 2-ethoxyethanol. R_F values are given for 22 different fat-soluble dyes, each with 16 variations of impregnating agent or eluent. N. E.

4040. **Detection of dyes possessing a *p*-phenylenediamine or a *p*-nitroaniline structure by means of spot tests.** F. Feigl and C. Costa Neto. *J. Soc. Dy. Col.*, 1956, **72**, 239–240.—When Bandrowski's base and azo dyes containing a *p*-phenylenediamine or a *p*-nitroaniline structure are fused with a dry mixture of Na formate and NaOH at 210° to 230°, *p*-phenylenediamine is formed by reductive cleavage. The diamine sublimes and the vapour reacts with an acetic acid soln. of aniline and alkali-metal persulphate to yield the indamine dye, phenylene blue. By the technique of spot-test analysis, it is possible to detect such dyes. The detection limits are in the range 5 to 10 μg. CHEM. ABSTR.

4041. **Estimation of sulphydryl [thiol] groups in wool by means of 1-(4-chloromercuriphenylazo)-2-naphthol. I. Experiments on intact fibres.** R. W. Burley (Nat. Chem. Res. Lab., S. Afr. Council Sci. Industr. Res., Pretoria, S. Africa). *Text. Res. J.*, 1956, **26**, 332–336.—The sulphydryl groups are estimated by determining the amount of 1-(4-chloromercuriphenylazo)-2-naphthol taken up by the wool from a standard soln. in formamide. Weighed purified wool samples (10 to 15 mg) of known H_2O content are placed in sealed tubes with 10 ml of the dye soln. (2 to 3 mg in 100 ml of formamide) and left at 30° for up to 25 days, with occasional shaking. The tubes are opened at intervals and examined until the filtered soln. reach a const. colour intensity. The sulphydryl-group concn. is expressed as micromoles per gram of dry wool. The colour reagent is standardised with glutathione in formamide. The determination is affected by the amount of H_2O and acid in the formamide, but with a pH of 7·8 to 8·2 and $\simeq$ 1% of H_2O the method is reproducible and sensitive.

II. Experiments on supercontracted and pulverised fibres. R. W. Burley. *Ibid.*, 1956, **26**, 336–341.—Data are given for sulphydryl-group determinations after supercontraction and after pulverisation on a large number of samples of wool from a small part of one merino fleece; the results were obtained over a period of six months. The mean values are in good agreement, although both sets of results show a large variation. The results are similar to those from intact fibres. A. M. SPRATT

4042. **Rapid total solids determination for concentrated ammonium bisulphite spent liquor.** R. W. Weaver (Rayonier Inc., Shelton, Wash., U.S.A.). *TAPPI*, 1956, **39** (1), 138A–139A.—The method consists in the determination of the sp. gr. of the liquor near its b.p. by means of a hydrometer. The temp. is recorded and surface scum is avoided by the addition of a film of a high-boiling low-gravity immiscible liquid to the surface of the test liquor. Charts are prepared correlating sp. gr., temp. and concn. The use of these permits the determination to be made by non-technical personnel with good accuracy and rapidity. L. S. ADLER

4043. **Determination of sulphide, thiosulphate and sulphite in white liquor. A study of TAPPI standard T 624 m-44 [1944].** B. Haegland and F. Loschbrandt (Norwegian Pulp and Paper Res.

Inst., Skøyen, Norway). *TAPPI*, 1956, **39** (2), 185A–187A.—The TAPPI method gave consistently high iodine consumptions. The source of error was found to be a side reaction, the oxidation of thiosulphate to sulphate according to the equation—

$S_2O_3^{2-} + 4I_2 + 10\,OH^- = 2SO_4^{2-} + 8I^- + 5H_2O$

instead of to tetrathionate. Oxidation to SO_4^{2-} was found to occur only at pH values greater than 5. At values lower than pH 5 only the oxidation to tetrathionate occurred. The difficulties are avoided if the test liquor is made weakly acid with acetic acid and then titrated directly with iodine soln.

L. S. ADLER

4044. **Determination of cellulosic and glass fibres in mixtures with asbestos.** C. Z. Carroll-Porczynski (British Belting and Asbestos Ltd., Cleckheaton, Yorks.). *J. Text Inst.*, 1956, **47** (12), T651–T652.—The amt. of cellulose in a mixture with asbestos and glass fibres is determined by the loss in wt. of a sample conditioned at 70° and 65% r.h. for 1 hr., after heating to 370° ± 10° for 1 hr., followed by cooling and conditioning as before. The sample is then re-heated to 800° for 1 hr., cooled, conditioned, and re-weighed. The asbestos is estimated by assuming that the second loss in wt. represents a standard loss of 13% of the total asbestos. The amt. of glass fibre is found by difference. Oil or other extraneous matter should be removed before ignition. Mineral carbonates or hydroxides may invalidate the estimation of the glass component.

A. M. SPRATT

4045. **A new method for the rapid determination of pure cellulose.** K. Seifert (Inst. Holztechnol. u. Faserbaustoffe, Dresden). *Papier*, 1956, **10**, 301–306.—A very rapid method is described for determining "pure" cellulose, which contains very small amounts of, or no, pentosans and mannans. Wood meal (200 to 50 meshes per sq. cm) (1 g), extracted with ethanol - benzene and air-dried, was heated for 0·5 hr. on a boiling-water bath with acetylacetone (6 ml), dioxan (2 ml) and HCl (d = 1·19) (1·5 ml). The mixture was filtered immediately, washed, stirred with methanol and treated successively with methanol, dioxan, hot H_2O, methanol and ether and dried at 105°. The Kürschner - Hoffer method applied to the same wood samples gave much higher results and the cellulose residues retained far more of the other wood components.

CHEM. ABSTR.

4046. **Infra-red spectrophotometric procedure for analysis of cellulose and modified cellulose.** R. T. O'Connor, E. F. DuPré and E. R. McCall (S. Reg. Res. Lab., New Orleans, La., U.S.A.). *Anal. Chem.*, 1957, **29** (7), 998–1005.—The potassium bromide disc technique can be used for the rapid, simple and reproducible measurement of the i.r. spectra of cotton fibres, yarns and fabrics. Applications show that chemical modification can be detected, the character of the modification identified, and the extent of the treatment estimated. A list of useful, characteristic absorption bands is given.

K. A. PROCTOR

4047. **Colorimetric determination of glycollate in carboxymethylcellulose.** M. Easterwood (Buckeye Cellulose Corp., Memphis, Tenn., U.S.A.). *Anal. Chem.*, 1957, **29** (6), 981–982.—Wash the sample (3 g) with 30 to 50-ml portions of 80% ethanol at 50° to 70° until the washings are chloride-free, and dilute the combined washings to contain 0·04 to 0·08 mg of Na glycollate per ml. To a 1-ml aliquot in a 25-ml flask add a 5% aq. soln. of chromotropic acid (disodium salt) (0·5 ml) and conc. H_2SO_4 (20 ml). Immerse in boiling water for 30 min., cool, make up to vol. with conc. H_2SO_4 and measure the purple colour spectrophotometrically at 570 mμ. Treat a reagent blank and standard soln. of glycollic acid (0·01 to 0·1 mg) in the same way. Beer's law is obeyed in the range stated. Results are given which show good reproducibility and satisfactory recovery of known amounts of glycollic acid added to carboxymethylcellulose. The chromotropic acid reagent should be freshly prepared and stored in a stoppered bottle in the dark, and the standard glycollic acid soln. (0·01% aq.) should be renewed after 30 days.

R. E. ESSERY

4048. **Determination of total sulphur in viscose.** T. N. Kleinert. *Textilrdsch.*, 1956, **11**, 402.—In comparing the total S contents of viscose by the H_2O_2 oxidation method with the gravimetric $BaSO_4$ method and the acid decomposition method which yields CS_2 and H_2S, it was found that the H_2O_2 method gave significantly higher S values than the other two methods. The reason for this discrepancy was traced to oxidative decomposition of cellulose resulting in higher alkali consumption. In the preferential formation of hemicellulose the oxidation products are low-mol.-wt. organic acids which are about proportional to the γ-cellulose content. The use of a subtractive constant is suggested which will bring the higher values of the H_2O_2 oxidation down to the correct values for S. CHEM. ABSTR.

4049. **The analysis of detergents; new method applicable to the alkali-metal salts of sulphated long-chain primary aliphatic alcohols.** J. A. Gautier and J. Renault. *Chim. Anal.*, 1957, **39** (5), 189–192.—The proposed volumetric and gravimetric methods for the determination of higher alkyl sulphate salts are based on pptn. of $(ROSO_3)_2Ni(NH_3)_4$ with excess of Ni^{2+} in aq. NH_3 soln. The precision is $\simeq \pm 1\%$. Short-chain compounds (up to C_{10}) are not pptd.; sodium and ammonium salts do not interfere. *Procedure*—Dissolve the sample ($\simeq$1 millimole) in H_2O (25 ml) with the aid of heat. Add 0·2 M aq. $NiCl_2$ (5 ml) and 10 N aq. NH_3 (10 ml), cool well, dilute to 50 ml with 10 N aq. NH_3 and mix. After 10 min., either filter and titrate an aliquot of the filtrate with 0·1 M EDTA (disodium salt), or collect the ppt. on a No. 4 sintered-glass crucible, wash free from Cl^- with a saturated ammoniacal soln. of the complex, and dry to constant wt. at 35°.

A. R. ROGERS

4050. **Analysis of coumarin compounds in citrus oils by liquid - solid partition.** W. L. Stanley and S. H. Vannier (Fruit and Veg. Chem. Lab., Agric. Res. Service, Pasadena, Calif., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1957, **40** (2), 582–588.—The seven substituted coumarins present in lemon oil can be separated by downward development on a chromatostrip prepared from silicic acid containing phosphors (*cf.* Miller and Kirchner, *Anal. Chem.*, 1954, **26**, 2002) and examination under u.v. light. Five of the spots are sufficiently separated to permit quant. recovery. By the use of 5-geranyloxycoumarin and 5:7-dimethoxycoumarin, standard curves of concn. *vs.* absorption at 320 to 330 mμ have been constructed. The presence of lime oil is detected by means of a new absorption peak at 270 mμ due to *iso*pimpinellin. A. A. ELDRIDGE

4051. **Carvone analysis by ultra-violet absorption.** R. H. Reitsema and W. E. Faas (Res. Lab., A. M. Todd Co., Kalamazoo, Mich., U.S.A.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1957, **46** (6), 381–383.—Carvone can be rapidly determined in spearmint oil by diluting the sample (0·1 ml) with methanol (15 ml) and measuring the extinction at 320 mμ in a 1-cm cell. The results are accurate within 1%. Comparison with the bisulphite method of assay suggests that results by the latter method are consistently 3 or 4% low. A. R. ROGERS

4052. **Examination of waxes.** C. L. Jones (Chiswick Products Ltd.). *Paint Technol.*, 1956, **20**, 361–364; 1957, **21**, 9–10, 13.—Methods for the determination of the m.p., setting-point, drop-point, softening-point, refractive index (particularly with regard to the detection of adulteration), density, molar refractivity, mol. wt., flash-point, hardness, tensile strength and ductility of waxes are reviewed, and their infra-red spectroscopy, X-ray diffraction analysis and chromatographic separation are discussed. L. A. O'NEILL

4053. **Characteristics of crude montan wax and their evaluation in assessing its quality. I. Determination of characteristics.** W. Schaack and D. Födisch (VEB Braunkohlenwerk "Gustav Sobottka", Röblingen am See). *Fette, Seif., Anstrichmitt.*, 1957, **59** (1), 30–35.—The ordinary methods for the determination of characteristics are not always applicable to crude montan wax. Methods that yield reproducible results in the determination of the following characteristics are described—acid, saponification and ester values, rising melting-point (rotating thermometer), residue on ignition, benzene-insoluble matter, acetone-insoluble matter at 20°, paraffin-insoluble matter and viscosity (90°). Attempts to use the following characteristics to indicate the quality of the wax were not successful—iodine value, light absorption, *iso*propyl alcohol-insoluble matter, bleaching test, refraction (molten wax), hydroxyl and carbonyl values. E. HAYES

4054. **Identification of epoxy resins.** H. W. Rudd and J. J. Zonsveld (Central Lab., Shell Petroleum Co., London). *Peint.-Pigm.-Vern.*, 1957, **33** (1), 35–37.—Earlier procedures, such as boiling the resin with *p*-phenylenediamine, required a lengthy preliminary separation of the other constituents. In the present method suggested by Foucry, 0·25 g of resin is dissolved in 25 ml of conc. H_2SO_4, and the soln. is divided into two parts. (*i*) Add 1 ml of 63% HNO_3 to 1 ml of the soln., set aside for 5 min. and pour into 100 ml of *N* NaOH. An orange - red coloration indicates the presence of an epoxy resin. (*ii*) Add 5 ml of Denigès soln. to 1 ml of the soln.; an orange - red coloration indicates an epoxy resin. The method is specific to epoxy resins made from diphenylolpropane and is positive with mixtures of epoxy resins and epoxy resin esters and with mixtures of these with urea - formaldehyde, melamine - formaldehyde, and phenolic resins, but negative with other resins, oils and solvents. F. J. M.

4055. **Isomerisation of linoleic, linolenic and other polyunsaturated acids with potassium *tert.*-butoxide and its application in the spectrophotometric estimation of these acids.** B. Sreenivasan and J. B. Brown (Ohio State Univ., Columbus, U.S.A.). *J. Amer. Oil Chem. Soc.*, 1956, **33** (11), 521–526.—Polyunsaturated acids with conjugated double bonds are normally estimated by measurement of the extinction exhibited at characteristic wavelengths. An alternative method is offered for the preliminary isomerisation of the acids, in which a soln. of K (5 g) in *tert.*-butyl alcohol (100 ml) is the reagent. A Pyrex-glass test-tube (150 mm × 25 mm) is flushed with N and into it are placed the reagent (10 ml) and the sample (about 0·1 g, in a small Pyrex-glass cup). An air-condenser, filled with N, is fitted to the mouth of the tube, which is then immersed in an oil bath at a temp. of 95°. The mixture is boiled for exactly 4 hr. when the tube is removed and placed in cold water to bring the contents to room temp. The soln. is transferred to a volumetric flask, washing in with methanol and finally diluting to 100 ml. The extinction of this soln. is measured at 233 and 268 mμ, and the content of linoleic and linolenic acids can be calculated from the results. More efficient conjugation is obtained by this method than with the usual KOH - glycol reagents. D. G. FORBES

4056. **Paper chromatography in the analysis of rubber compounds.** R. Miksch and L. Prölss. *Deut. Kautschuk-Ges. Vortragstag., Hamburg*, 1956, 35 pp.—Methods are described for the separation and identification of acid and basic accelerators and antioxidants by paper chromatography. CHEM. ABSTR.

4057. **Determination of antioxidants [in rubber].** J. W. H. Zijp (Kautschuk-Forsch.-Inst. T.N.O., Delft, Holland). *Deut. Kautschuk-Ges. Vortragstag., Hamburg*, 1956, 4 pp.—The paper-chromatographic technique (*Kautsch. u. Gummi*, 1955, **8**, WT160) with specially acetylated paper (*Anal. Abstr.*, 1955, **2**, 3526) is applied to extracts of compounds or vulcanisates containing phenyl-2-naphthylamine (**I**) or diphenyl-*p*-phenylenediamine (**II**). To identify **I**, the appropriate spot is extracted for 1 to 1·5 hr. in the dark in 96% ethanol, treated with diazotised sulphanilic acid and determined colorimetrically at 500 mμ. The spot containing **II** is treated similarly with benzene, oxidised with a 5% soln. of benzoyl peroxide and determined at 450 mμ. CHEM. ABSTR.

4058. **Determination of unsaturation in butyl rubber using carbon-14-labelled isoprene.** L. R. McNall and L. T. Eby (Esso Research and Engineering Co., Linden, N.J., U.S.A.). *Anal. Chem.*, 1957, **29** (6), 951–954.—Butyl rubber of known saturation was prepared from ^{14}C-labelled isoprene and was used to measure the efficiency of the drastic iodine - mercuric acetate and the ozone addition methods for the determination of the unsaturation of butyl rubber. The amount of diolefin entering the polymer was determined by isotope tracer techniques, and for the calculation of unsaturation it was assumed that there was one double bond for each molecule of isoprene entering the polymer. The commonly used iodine - mercuric acetate method was found to be reliable, but the result must be increased by 15% to give accurately the isoprene content of the copolymer; the iodine equivalent is therefore 2·61 instead of 3 for this method. The procedure involving ozonisation of the polymer gave poor results ($\simeq$ 45% recovery). G. P. COOK

4059. **Statistical control in analytical chemistry. Application to Devarda's method for the determination of nitrogen in nitrocelluloses.** Y. Lacroix and N. Bugat (Service des Poudres, France). *Chim. Anal.*, 1957, **39** (5), 180–183.—Control charts have been used in the interpretation of the results of daily checks on the concentration of an H_2SO_4 sample with Na_2CO_3 (by titration) and with KNO_3 (by Devarda's method) and on the percentage of nitrogen in a sample of gun-cotton. The precision, expressed as limits of error (P = 0·997), was ±0·1%, ±0·2% and ±0·23%, respectively. Evidence is presented that the amount of nitrogen in gun-cotton falls on storage. A. R. ROGERS

4060. **Infra-red quantitative analysis data.** *Anal. Chem.*, 1957, **29** (10), 1551–1554.—The following data have been published under the co-operative programme between *Analytical Chemistry* and the Coblentz Society of the U.S.A. **Determination of phenol, *o*-*tert.*-butylphenol, 2:4-di-*tert.*-butylphenol and 2:4:6-tri-*tert.*-butylphenol in *tert.*-butylphenol mixtures,** R. T. Scheddel and L. R. Kiley. **Determination of phenol, 2-chlorophenol, 4-chlorophenol and 2:4-dichlorophenol in monochlorophenols,** R. T. Scheddel. **Determination of ethylbenzene, styrene and vinyl cyanide in co-monomer mixtures,** L. R. Kiley. **Determination of 1:2-epoxy-2-methylpropane in mixed epoxybutanes,** L. R. Kiley. **Determination of 2:4-dichlorophenol, 2:6-dichlorophenol, 2:4:6-trichlorophenol, 2:3:4:6-tetrachlorophenol and pentachlorophenol in higher chlorophenol mixtures,** R. T. Scheddel and L. R. Kiley. **Infra-red analysis of isomeric vinyltoluene mixtures with low ortho content,** N. Hadden and W. F. Hamner. **Determination of chloropicrin in methyl bromide,** R. T. Scheddel and L. R. Kiley. **Infra-red analysis of isomeric vinyltoluene mixtures,** N. Hadden and W. F. Hamner. **Determination of styrene and α-methylstyrene in co-monomer mixtures,** L. R. Kiley.

Ibid., 1957, **29** (11), 1717-1718.—**Analysis of *tert.*-butylphenol mixtures,** R. P. Curry. **Analysis of chlorobenzene mixtures,** R. L. Hudson. **Determination of diethyl diethylmalonate in diethyl ethylmalonate,** W. H. Washburn. **Analysis of hexachloro-*cyclo*hexane mixtures by infra-red absorption,** R. L. Hudson.

See also Abstracts 3868, 3892, 3893, 3914, 4137, 4138, 4220.

4.—BIOCHEMISTRY
INCLUDING DRUGS, FOOD, SANITATION, AGRICULTURE

Blood, Bile, Urine, etc.

4061. **Spectrofluorimetric study of compounds of biological interest.** D. E. Duggan, R. L. Bowman, B. B. Brodie and S. Udenfriend (Nat. Heart Inst., U.S. Dept. Health, Bethesda, Md., U.S.A.). *Arch. Biochem. Biophys.*, 1957, **68** (1), 1–14.—A survey is made of the fluorescence characteristics of 55 biologically important compounds by means of one experimental and two commercial spectrophotofluorimeters. For each compound, wavelengths of max. activation and fluorescence, optimum pH for development of fluorescence, and an arbitrary measure of ultimate sensitivity are given. Many of the compounds studied had not previously been reported as fluorescing in soln. Practical aspects of the application of the method to qual. and quant. analysis are discussed. W. H. C. SHAW

4062. **Determination of urinary fluoride.** D. F. Adams, R. K. Koppe and D. J. Mayhew (Washington State Inst. of Technol., State College of Washington, Pullman, U.S.A.). *Anal. Chem.*, 1957, **29** (7), 1108–1110.—The Smith and Gardner modification (*Arch. Biochem.*, 1950, **29**, 311) of the salt - acid - thorium titration of Williams (*Analyst*, 1946, **71**, 175) is used to eliminate the necessity for removal of Cl^- by silver, and to improve recovery by reference of results to a standard curve prepared by distillation of known amounts of F^- from urine. The sample (25 ml) is treated with CaO (1 g, low in F), evaporated to dryness and ashed in a muffle-furnace at 600° for 30 min. The cooled ash is dissolved in 72% $HClO_4$ and steam-distilled at 137°, 400 ml of distillate being collected. An aliquot containing < 100 μg of F^- is made up to 80 ml, treated with 1% hydroxylamine hydrochloride, an acid soln. of alizarin red S, and 5% NaCl. The pH is adjusted to 2·90 with HCl and the mixture is titrated with acid $Th(NO_3)_4$ soln. (0·0268%) until the colour matches that of a specified permanent inorganic colour standard. Results for the recovery of known amounts of F^-, up to 45 μg, from bovine urine by this method show better mean recoveries than those by two other methods, with much the same range and standard deviation.
R. E. ESSERY

4063. **Determination of radium-226, actinium-227 and thorium-228 in human urine.** H. W. Kirby and R. M. Brodbeck (Mound Lab., Miamisburg, Ohio, U.S.A.). *U.S. Atomic Energy Comm.*, Rep. MLM–1003, 1954 (issued 9.4.56), 21 pp.—These isotopes and their decay products may occur in the urine of lab. workers who process neutron-irradiated ^{226}Ra. The procedure for determining ^{226}Ra, ^{224}Ra and ^{223}Ra is based on the quant. insolubility of barium nitrate in 80% HNO_3. The Ra isotopes are co-pptd. on the $Ba(NO_3)_2$ and the α-activity is differentially determined. The procedure is completed for the determination of ^{226}Ra when that isotope and its decay products are present alone. Actinium and Th are quant. co-pptd. on cerium phosphate, but the results are erratic and Po, Bi and Pb isotopes are carried down at the same time, causing interference.
CHEM. ABSTR.

4064. **Low-level polonium determination of tissue and urine.** S. C. Black (Univ., Rochester, N.Y., U.S.A.). *U.S. Atomic Energy Comm.*, Rep. UR–463, 1956, 124 pp.—Methods were developed for the analysis of up to 50 g of soft tissue and bone and litre volumes of urine for Po of the order of 1 dpm above background. NUCLEAR SCI. ABSTR.

4065. **Estimation of the level of blood alcohol from analysis of breath. II. Use of rebreathed air.** R. N. Harger, R. B. Forney and R. S. Baker (Indiana Univ. School of Med., Indianapolis). *Quart. J. Stud. Alc.*, 1956, **17**, 1–18.—Analyses for alcohol were conducted with rebreathed air, finger-tip capillary blood and cubital-vein blood taken almost simultaneously from 31 human subjects 1 to 3 hr. after ingestion of whisky in doses providing 0·69 to 1·70 (generally 1·03) g of alcohol per kg of body wt. During the first 70 min. after drinking, the alcohol level of the capillary

blood averaged 7·5% above that of venous blood; later samples showed no significant difference between blood from the two sources. The rebreathed air to blood-alcohol ratio was 1:2100. This ratio proved reliable for the estimation of blood-alcohol level from that of rebreathed air. Modifications of the earlier "Drunkometer" method are described. CHEM. ABSTR.

4066. **Colorimetric procedure for the determination of blood ammonia.** D. G. Nathan and F. L. Rodkey (Harvard Med. Sch., Boston, Mass., U.S.A.). *J. Lab. Clin. Med.*, 1957, **49** (5), 779–785.—In the method described, the sample (3 ml) is treated with trichloroacetic acid and, after centrifugation, the NH_3 in an aliquot of the clear supernatant liquid is liberated in a micro-diffusion apparatus by addition of excess of aq. K_2CO_3 soln. The NH_3 is collected on a glass rod moistened with *M* citric acid, and determined colorimetrically with ninhydrin. Results are reproducible and recovery of added NH_3 is quant. The venous blood level of normal fasting human subjects is 0·77 ± 0·28 μg of ammonia-N per ml. W. H. C. SHAW

4067. **A new colorimetric reagent for micro-determination of ammonia.** W. E. Stone (Dept. Physiol., Sch. Med., Univ. Wisconsin, Madison, U.S.A.). *Proc. Soc. Exp. Biol. Med.*, 1956, **93**, 589–591.—The range of the method is 0·05 to 0·5 micromole. Conway's micro-diffusion method was used to separate NH_3 from interfering substances. The NH_3 was oxidised by adding BrO^- and the excess of BrO^- was estimated by its power to decolorise phenosafranine. This procedure has been applied to brain tissue and blood, and to the estimation of glutamine; also to the direct estimation of non-protein N without micro-diffusion.
NUTR. ABSTR. AND REV.

4068. **Identification of thiobarbituric acids in urine by paper chromatography.** W. Dietz and K. Soehring (Pharmakol. Inst., Univ. Hamburg, Germany). *Arch. Pharm., Berlin*, 1957, **290** (2), 80–97.—Short- and ultra-short-acting thiobarbiturates and some of their degradation products can be identified in human and dog urine by means of ascending uni-dimensional chromatography. The method of Hubner and Pfeil (*Anal. Abstr.*, 1955, **2**, 174) is used for development. For the detection of the spots, two reagents are used—(*i*) a soln. of 5 g of cryst. $CuSO_4$ in 100 ml of methanol to which is added 3 ml of diethylamine, and (*ii*) a filtered satd. aq. soln of mercurous nitrate. Six commercial thiobarbiturates show R_F values between 0·66 and 0·75. Metabolites give lower values. J. WATT

4069. **Determination of carotene in faeces.** Tsuyuko Kawaguchi (Kitasato Inst., Tokyo). *Vitamins, Japan*, 1955, **9**, 388–390.—For the determination of carotene (**I**) in faeces the use of alumina for chromatography was found to be unsuitable, because the **I** fraction contains other pigments which cause high values for **I**. For this purpose $Ca(OH)_2$ is adequate. Saponification is not necessary for determining **I** alone.
CHEM. ABSTR.

4070. **Determination of vitamin A in faeces.** Tsuyuko Kawaguchi (Kitasato Inst., Tokyo). *Vitamins, Japan*, 1956, **10**, 8–11.—In determining vitamin A (**I**) in faeces by weakly activated alumina by chromatography, it can sometimes occur that pigments in faeces appear not only in a light petroleum fraction but also in a 1·25% acetone - light petroleum fraction. This interference with **I** determination can be avoided by the use of 0·5% acetone - light petroleum mixture as eluting agent for **I**. In cases where much pigment is present in faeces **I** can appear in the light petroleum fraction and, in this case, a complete separation of **I** from carotenoids is difficult to attain. The Carr - Price values of carotenoids are relatively so low that the correction due to carotenoids is, in general, scarcely necessary. CHEM. ABSTR.

4071. **Hydrogenation *versus* chromatography in the estimation of tocopherol in calf plasma.** M. W. Dicks, J. E. Rousseau and H. D. Eaton (Storrs Agric. Exp. Sta., Conn., U.S.A.). *J. Dairy Sci.*, 1957, **40** (5), 590–591.—A comparative study is made of hydrogenation and chromatography on Floridin earth for the removal of carotenoids before the determination of tocopherol by the reaction of Emmerie and Engel. No significant difference in results by the two methods was found, but the hydrogenation procedure was quicker and simpler.
W. H. C. SHAW

4072. **Interference with sugar test in urine by tetracycline (Hostacyclin).** A. Häussler (Farbwerke Hoechst A.-G.). *Arch. Pharm., Berlin*, 1957, **290** (2), 25–29.—Patients receiving tetracycline eliminate the drug in various quantities in the urine; it interferes with the usual qual. urine sugar tests (Nylander, Fehling, Trommer, Moore) and gives false positive results. Polarimetric methods are also unreliable. In the presence of tetracycline, urine sugar must be determined by the fermentation method. J. WATT

4073. **The isolation of carbon as barium carbonate in studies with carbon-14.** L. H. Adcock (Howards of Ilford Ltd., Ilford, Essex, England). *Analyst*, 1957, **82**, 449–452.—The apparatus described and illustrated and the method were designed for metabolic studies in which ^{14}C compounds were used (Adcock *et al.*, *Nature*, 1956, **177**, 329), but they are suitable for general use. The material is oxidised by means of a chromic acid mixture (Van Slyke, *Anal. Abstr.*, 1955, **2**, 931), the CO_2 evolved is absorbed in NaOH soln. and pptd. as $BaCO_3$, in which form it is weighed. Quoted results of the application of the method to glucose and sorbitol and to mixtures of glucose or succinic acid or potassium hydrogen phthalate with blood or urine indicate recoveries ranging from 98·4 to 101·7%. Application of the method to the determination of CO_2 in expired air is described. A. O. JONES

4074. **Differential thermal analysis of some polyglucosans.** Hirokazu Morita (Chem. Div., Canada Dept. of Agric., Ottawa). *Anal. Chem.*, 1957, **29** (7), 1095–1097.—The author discusses the thermographic curves obtained by a method previously described (Morita and Rice, *Anal. Chem.*, 1955, **27**, 336), with 75-mg vacuum-dried samples and a heating rate of 10° per min. Glycogens from rabbit liver, guinea-pig liver, hog roundworm and Ascaris give thermograms that show marked differences. These differences are at variance with methylation and periodate oxidation studies, which point to the same repeating unit in all these glycogens, and it is suggested that they are associated with structural variations in the glycogens of different origin, such

as degree of multiple branching, or the presence of glycosidic linkages other than 1:6 or 1:4. Thermograms are given for *Constantinea floridean* starch, Euglenaceae paramylon and laminarin, and the effect of moisture on rice-starch thermograms is discussed. R. E. ESSERY

4075. **A new method for the determination of inulin.** L. Costabile and E. Sanseverino (Ist. Chim. Biol., Univ. Naples). *Boll. Soc. Ital. Biol. Sper.*, 1956, **32**, 107–108.—Citrated plasma (1 ml) is added to satd. aq. picric acid soln. (4 ml), shaken, allowed to stand for 15 min. and centrifuged. The deproteinised centrifugate (1 ml) is added to water (3 ml) in a Folin tube and hydrolysed by boiling for 60 min., cooled, added to 1 ml of Na_2CO_3 soln. (15 g in 100 ml of water), made up to 4 ml with water and boiled again for 15 min. After cooling, the soln. is diluted as required with water and compared photometrically or colorimetrically with standard soln. of fructose in ⅛-satd. picric acid. NUTR. ABSTR. AND REV.

4076. **Determination of inulin in the presence of high glucose concentrations by the resorcinol - thiourea procedure after alkali-autoxidation of the glucose.** T. U. Ullman and L. Ullman (Rothschild-Hadassah Univ. Hosp., Jerusalem, Israel). *J. Lab. Clin. Med.*, 1957, **49** (5), 793–795.—The conditions required for the destruction by aq. NaOH of glucose in samples obtained in glomerular filtration rate experiments with inulin are studied. It is concluded that provided the inulin used does not contain more than 13% of alkali-labile fractions no destruction of inulin takes place in the presence of 0·3 to 0·4 mg of glucose per ml. Under these conditions inulin can be determined satisfactorily by the resorcinol - thiourea method. W. H. C. SHAW

4077. **New colour reaction for the determination of aldopentose in presence of other saccharides.** Z. Dische and E. Borenfreund (Columbia Univ., New York, U.S.A.). *Biochim. Biophys. Acta*, 1957, **23** (3), 639–642.—The modified phloroglucinol reaction described makes possible the differentiation between aldo- and keto-pentoses and the determination of small amounts of pentoses and their nucleotides in the presence of larger amounts of other sugars. *Procedure*—To 0·4 ml of test solution containing 4 to 40 μg of pentose per ml add 5 ml of a freshly prepared mixture of 110 ml of glacial acetic acid, 2 ml of HCl (sp. gr. 1·19), 1 ml of 0·8% glucose and 5 ml of 5% phloroglucinol solutions. Mix by shaking, immerse the mixture for 15 min. in boiling water and then cool under running water. Measure the extinctions at 552 mμ and 510 mμ against a blank prepared with water instead of the test solution. Calculate the amount of pentose from the extinction at 552 mμ for pure solutions or, in the presence of other sugars, from the difference in extinctions at the two wavelengths. Calibrate with standards treated similarly. W. H. C. SHAW

4078. **Determination of sugar ratios by chromatography and direct photometry.** S. M. Martin (Div. of Appl. Biol., N.R.C., Ottawa, Canada). *Chem. & Ind.*, 1957, (25), 823–824.—The technique of the direct measurement of transmittance density of spots developed by $AgNO_3$ soln. on a paper chromatogram is described. Relative reducing power is constant and thus it is not necessary to calibrate each chromatogram. E. G. CUMMINS

4079. **New reagents for paper chromatography.** F. S. Gómez Carcedo. *Farmacognosia*, 1956, **16**, 113–141.—New sensitive reagents for uronic acids, sugars and amino sugars have been developed: (*a*) 0·5% aminoazobenzene in 96% ethanol (4 ml), aniline (1 ml), 96% ethanol satd. with $CaCl_2$ (20 ml), and 96% ethanol to make 100 ml; (*b*) 0·5% *p*-dimethylaminoazobenzene in 96% ethanol (20 ml), 10% *p*-aminophenol (5 ml), 96% ethanol satd. with boric acid (3 ml), and 96% ethanol satd. with $CaCl_2$ (2 ml). A sensitivity of 0·000015 μg of glucosamine hydrochloride is claimed for reagent (*a*). SUGAR IND. ABSTR.

4080. **Identification and assay of serotonin [5-hydroxytryptamine] in brain.** D. F. Bogdanski, A. Pletscher, B. B. Brodie and S. Udenfriend (Nat. Heart Inst., Bethesda, Md., U.S.A.). *J. Pharmacol.*, 1956, **117**, 82–88.—A fluorimetric method for the determination of 5-hydroxytryptamine (**I**) is described; it involves the use of a spectrofluorimeter which can activate and measure emitted fluorescence continuously from 250 to 650 mμ. **I** is activated maximally at 295 mμ and emits fluorescent light which shows a max. at 550 mμ. The method can be applied to other tissues. CHEM. ABSTR.

4081. **Separation and identification of pyrophosphates in bone tissue.** P. Cartier. *Compt. Rend.*, 1956, **243** (14), 982–985.—Pyrophosphates can best be separated from a trichloroacetic acid soln. of dry powdered bone by adsorption on a column of quaternary ammonium anionic resin and aminophenol (De-Acidite, 120 to 200 mesh, Cl^- form), followed by elution with 0·02 *N* HCl (to remove other phosphates) and then with 0·1 *N* HCl. The presence of $P_2O_7^{4-}$ in the final fraction is confirmed by acid or enzyme hydrolysis, radioactive analysis, and paper electrophoresis or chromatography. The content of $P_2O_7^{4-}$ in bone is ≃ 0·5% of the total P. W. J. BAKER

4082. **Paper chromatography of phospholipids on silicic acid impregnated glass-fibre filter-paper.** J. W. Dieckert and R. Reiser (Texas Agric. Exp. Sta., U.S.A.). *J. Amer. Oil Chem. Soc.*, 1956, **33** (11), 535–537.—A method that gives reproducible results has been developed for the satisfactory separation of lysolecithin, lecithin, sphingomyelin and phosphatidylethanolamine. A soln. of the lipid (0·1%) is spotted (in amounts equiv. to 10 μg of lipid) on to glass-fibre filter-paper impregnated with silicic acid and allowed to reach equilibrium with the solvent during 30 min. The chromatogram is run for 1 to 1·5 hr., with the ascending technique and methanol - diethyl ether (1:1) as solvent. It is then possible to locate the spots and to identify functional groups with the following reagents—(*a*) H_2SO_4 (1:1), followed by warming; (*b*) ninhydrin soln. (0·1% in citrate buffer), followed by warming at 100°; (*c*) modified Dragendorff reagent; (*d*) $KMnO_4$ soln. (1%). D. G. FORBES

4083. **Colorimetric method for the estimation of nucleic acids in tissues.** C. Costache, E. Nistor, C. Tanăsescu, E. Mico and A. Havas. *Stud. Cercet. Chim., Cluj*, 1956, **7** (1–4), 167–174.—After the removal of phospholipids and acid-soluble phosphates, the tissue is treated with trichloroacetic acid to extract total nucleic acids. Ribonucleic acid (**I**) and total nucleic phosphorus are determined colorimetrically. A mixture of Nile blue soln.

(0·01%) and methyl orange soln. (0·01%) is used as a permanent artificial standard for **I**. In this way 0·15 mg of **I** can be estimated. The difference between the total nucleic phosphorus and that due to **I** gives the phosphorus corresponding to thymonucleic acid. An accuracy of ± 0·2% is claimed. The method is of general application, in particular to cancer tissue. H. SHER

4084. **The determination of amino acids by paper chromatography.** Y. Bito (Univ. Osaka, Japan). *J. Biochem., Japan*, 1956, **43**, 523–529.—Details of a satisfactory procedure are given in which ascending chromatography and the solvent *n*-butanol - acetic acid - water (4:1:2) are used. N. E.

4085. **The separation of basic amino-acids by chromato-electrophoresis on paper.** S. Gerlaxhe, J. Casimir and M. Renard (Lab. de Chim. Gén., Inst. Agronom. de l'État, Gembloux, Belgium). *Bull. Soc. Chim. Belg.*, 1957, **66** (3–4), 251–255.—A good separation of ornithine, lysine, histidine, arginine, glycine, threonine, β-alanine, aspartic acid and glutamic acid is obtained by paper chromatography on S. & S. 2043b paper with phenol saturated with a buffer at pH 5·6, of ionic strength 0·05, followed by electrophoresis at right angles in the same buffer, with a Pleuger "chromatoélectrorhéophor" apparatus. E. J. H. BIRCH

4086. **Quantitative determination of amino acids in undesalted hydrolysates by buffer filter-paper chromatography.** B. E. Baker and N. A. Khan (Dept. of Agric. Chem., Macdonald College, Que., Canada). *J. Sci. Food Agric.*, 1957, **8** (4), 217–222.—The technique described includes the use of five new solvent systems. Results obtained with casein are in good agreement with published results. H. B. HEATH

4087. **Chromatographic analysis of amino acids excreted in the urine.** J. Noworytko and M. Sarnecka-Keller (Zakl. Chem. Fizjol. A.M., Cracow). *Acta Biochim. Polon.*, 1956, **3**, 309–321.—Urine was desalted by passage through a column of polystyrene resin, Zeo-Karb 225, in which all inorganic cations and amino acids were retained, and through which inorganic anions easily passed. The amino acids eluted from the column with 2 *N* aq. NH_3 were vacuum-dried, dissolved in water and analysed by paper chromatography, with isatin as colour developer. NUTR. ABSTR. AND REV.

4088. **3:4-Dimethylhexane-2:5-dione as a colour reagent for biological preparations and as a reagent for amino acids.** M. Lüdicke (Zoolog. Inst. Univ. Heidelberg, Germany). *Z. Naturf.*, 1956, **11b** (9–10), 525–529.—Pure amines react with 3:4-dimethylhexane-2:5-dione to give colourless products or yellow crystals, but urea, polyamides and amino acids give red colours. Addition of Na_2HPO_4 intensifies the colour. Formaldehyde and sugars do not give colours with the reagent. E. KAWERAU

4089. **Quantitative determination of 0·5 to 5 μg of amino-acid nitrogen on paper chromatograms and in solution.** H. L. Kornberg and W. E. Patey (Med. Res. Council, Oxford Univ., England). *Biochim. Biophys. Acta*, 1957, **25** (1), 189–193.—Interference by NH_4^+ in the colorimetric determination of amino acids with ninhydrin is eliminated by preferential adsorption of the NH_4^+ on prepared Dowex-50 resin. By this method, 0·5 μg of α-amino N can be determined to within ± 5% and 1·5 to 5·0 μg to within ± 2%. The method is also suitable for the direct determination of amino-acid N in soln. such as protein hydrolysates. *Procedure*—Cut out the areas of the amino-acid spots located by fluorescence (or autoradiography when appropriate) on paper chromatograms and shred into a stoppered test-tube containing 150 mg of dry Dowex-50 resin, previously washed and equilibrated with 0·2 *M* Na citrate buffer, pH 5·0, before drying. Prepare a blank by treating a similar portion of the paper free from amino acids in the same way. Add 2 ml of 0·05 *M* Na citrate buffer (pH 5·0), close the tube, mix well and allow to stand for 1 to 2 hr. Dilute aliquots (0·5 to 1 ml) of the soln. to 1·5 ml with 0·2 *M* citrate buffer and complete the determination of amino acid by the method of Yemm and Cocking (*Anal. Abstr.*, 1955, **2**, 2181). Protein hydrolysates are evaporated to dryness over H_2SO_4 in washed N and the dry material is dissolved in 2·0 ml of 0·05 *M* citrate buffer. Aliquots of 0·05 to 1·0 ml are diluted to 2 ml with citrate buffer and treated with Dowex-50 resin as described above. W. H. C. SHAW

4090. **Paper chromatography of amino acids, sugars and acids.** G. Högström (Dept. Physiolog. Chem., Wenner Grens Inst., Stockholm, Sweden). *Acta Chem. Scand.*, 1957, **11** (4), 743–745.—The common solvents used in chromatography for the separation of amino acids, sugars, etc., in spite of having good resolving power, are often objectionable on account of their toxic properties and liability to chemical change. Ethyl methyl ketone is suggested as a suitable alternative to such solvents as phenol and collidine, and in conjunction with acetone, water and formic acid a high degree of resolution of the compounds can be attained. For the analysis of mixtures of the amino acids, the sample soln. is spotted on to a chromatographic strip and the experiment is run for 30 hr. with a solvent composed of a mixture of ethyl methyl ketone - acetone - water (3:1:0·6) (**I**). The paper is dried and the positions of proline and valine are determined by developing a control strip with ninhydrin. The upper section of the chromatogram carrying proline and the slower-moving acids is attached sideways to a second piece of paper so that these acids can be resolved by development in a direction at right angles to the original with the same mixture of solvents in the proportion 3:1:1 with the addition of 0·1 part of formic acid. Solvent **I** can be used for the separation of sugars; for organic acids, a suitable solvent is ethyl methyl ketone - water - acetone - formic acid (80:12:6:2). During the analysis of natural material, salts will detract from the efficiency of the separations and an apparatus is illustrated which suitably removes this interference. The test soln. is placed on a paper strip at about 5 cm from one end. The strip is enclosed horizontally between two pieces of glass, and the end carrying the sample is bent down into a trough containing a mixture of acetone, water and aq. NH_3 (7:3:0·4), while the further end protruding from the glass just touches the chromatography strip at the point at which the sample drop is to be started. As the solvent is drawn on to the desalting strip, the amino acids are separated and move towards the second paper to which they become transferred. A stream of warm air is used to dry off the eluting solvent. Quant. separation is achieved with 8-hr. elution through a 20-cm desalting strip. D. G. FORBES

4091. **Ion-exchange chromatography of amino acids and peptides. I. A new method of determination for basic amino acids on a carboxylic acid resin.** Shinichi Ishii (Tokyo Univ.). *J. Biochem., Japan*, 1956, **43**, 531–537—A column of Amberlite IRC-50 (XE 64) is equilibrated at pH 5·95 to 6·00 with the eluent (2 vol. of 0·575 *N* Na citrate buffer, pH 5·95 to 6·00, with 1 vol. of 0·236 *N* sodium phosphate buffer, pH 5·95 to 6·00). A total vol. of 52 ml is collected in 0·8-ml portions, the colour intensity of each fraction being measured at 570 mμ after treatment with ninhydrin at pH 5. N. E.

4092. **Polarimetric assay of cysteine after oxidation to cystine.** R. Willemart (Services de Rech. Roussel-Uclaf, Paris-Romainville, France). *Ann. Pharm. Franc.*, 1956, **14** (11), 718–719.—The small rotatory power of cysteine (+ 7·6° in *N* HCl) is enhanced by oxidation to cystine (− 220° in *N* HCl). *Procedure*—Cysteine (0·25 g) in 2·5 ml of *N* HCl is treated drop by drop with 0·1 *N* iodine to a yellow colour, which is discharged with 0·01 *N* $Na_2S_2O_3$. The soln. is made up to 25 ml with *N* HCl, and the rotation is measured in a 2-dm tube, with the sodium D-line. E. J. H. Birch

4093. **Determination of L-glutamic acid by use of L-glutamic acid decarboxylase from *Mycobacterium phlei*.** Y. S. Halpern and N. Grossowicz (Hebrew Univ.-Hadasseh Med. Sch., Jerusalem). *Proc. Soc. Exp. Biol. Med.*, 1956, **91** (3), 370–373.—The method depends on the measurement in a Warburg manometer of the CO_2 evolved in the decarboxylation of L-glutamic acid by a preparation of *M. phlei* with decarboxylase activity. The preparation had no detectable activity towards 18 other amino acids and no glutaminase or glutamo-racemase activity. N. E.

4094. **Evaluation of the Sakaguchi reaction for quantitative determination of arginine.** D. D. Gilboe and J. N. Williams, jun. (Dept. Biochem., Univ. Wisconsin, Madison, U.S.A.). *Proc. Soc. Exp. Biol. Med.*, 1956, **91** (4), 535–536.—The Sakaguchi reaction (*J. Biochem., Japan*, 1925, **5**, 25) has been studied and the best conditions are reported. The method is entirely satisfactory for determining arginine over the range 0 to 30 μg. The coeff. of variation of the method is ± 0·5%. N. E.

4095. **Determination of the carbohydrates in the glycoproteins and mucoproteins of cerebrospinal fluid.** E. Roboz, R. R. Apostol, A. M. Luft and W. C. Hess (Georgetown Univ., Med. Sch., Washington, D.C., U.S.A.). *J. Lab. Clin. Med.*, 1957, **49** (5), 796–801.—Methods are described for the determination of the hexose and hexosamine content of mucoproteins, glycoproteins and of α-glycoprotein in c.s.f. After preliminary separation by a modification of the procedure of Weimer and Moshin (*Amer. Rev. Tuberc.*, 1953, **68**, 594), the pptd. proteins are analysed for hexose and hexosamine by the method described earlier (*Proc. Soc. Exp. Biol. Med.*, 1955, **89**, 691), and also for tyrosine. The ratio of results obtained on c.s.f. to those on blood serum is considered of importance in abnormal neurological conditions, and the significance of this is discussed. W. H. C. Shaw

4096. **Agar electrophoresis. I. Simple clinical method for the analysis of serum proteins.** K. V. Giri (Indian Inst. of Sci., Bangalore). *J. Indian Inst. Sci., A*, 1956, **38** (3), 190–199.—Agar is claimed to be superior to paper as a medium for the electrophoresis of serum proteins in that there is better and more rapid resolution, the stained bands are more easily evaluated, no protein trailing is produced and there is a greater capacity than with either paper or starch. *Procedure*—Agar (2 g) is autoclaved in water (100 ml) at 15 lb pressure for 30 min. Equal vol. of this 2% agar gel and buffer of ionic strength 0·10 [barbitone sodium (29·43 g), Na acetate trihydrate (19·43 g) and 0·1 *N* HCl (180 ml) made up to 3 litres] are mixed. The warm buffered gel (10 ml) is cast in a Perspex frame (30 cm long × 3·4 cm wide × 1·2 mm thick) supported on a glass plate which may have Cellophane or polyester film as a base for the gel. Whatman No. 3 paper strips (8 cm × 4 cm) are placed at each end, extending 0·5 cm into the frame. When the gel is set, the serum (10 μl) is applied to the centre on a 2-mm-wide paper strip and a similar frame and glass plate are superimposed. The paper strips dip into electrode vessels containing buffer (300 ml, pH 8·6, ionic strength 0·05). Optimum separation is achieved with a 3 to 5-hr. run at 200 to 300 V and 8 to 9·5 mA. The components may be located by coagulation with trichloroacetic acid, or, when completely dry, by immersion in Amido black 10B soln. (0·5% in methanol - acetic acid - water) (4:1:5) for 20 min., followed by two washings in glacial acetic acid - methanol (9:1), and drying at room temp. A quant. evaluation of the stained protein components may be made either directly or by elution and colorimetry of the dye with 0·05 *N* NaOH. D. G. Lloyd

4097. **Staining of the serum beforehand as a simple and rapid method for estimating the ratio of β- to α-lipoproteins.** M. Mancini and A. Orengo (Ist. Fisiol. Umana, Univ. Naples). *Boll. Soc. Ital. Biol. Sper.*, 1956, **32**, 649–652.—The method depends on staining the serum first by adding to 1 ml of serum 0·1 ml of satd. soln. of Sudan black B, Merck 51545, in 95% ethanol. The mixture is centrifuged for 30 min. at 3000 r.p.m. and 0·1 ml is then separated by electrophoresis; the strips are dried quickly and cut along the max. front of the β-lipoproteins. The fractions are eluted in 7 ml of ethanol - acetic acid (4:1 by vol.) for 60 min. and estimated at 595 mμ. The standard error of the α-fraction was ± 1·95%. Nutr. Abstr. and Rev.

4098. **Simple, rapid method for quantitative determination of salivary amylase.** C. K. Claycomb, M. N. McChesney and M. L. Snyder (Univ. Oregon, Portland, U.S.A.). *J. Dent. Res.*, 1956, **35**, 391–398.—The determination is made in test-tubes (16 mm × 150 mm). To 19 ml of a 1·28% aq. soln. of sol. starch (indicator grade) add 0·5 ml of NaCl - phosphate buffer (0·2% NaCl in Na_2HPO_4 - KH_2PO_4 buffer of pH 7), bring to a temp. of 40° in a water bath, add 0·1 ml of saliva (refrigerated but not frozen), and mix by inversion. Keep in the bath for exactly 5 min., then terminate enzyme activity and develop the colour by addition of 1 ml of a reagent prepd. by mixing (*a*) 5 ml of an aq. soln. containing 3 g of reagent-grade KI and 0·6 g of resublimed iodine per 100 ml, (*b*) 25 ml of 1·0 *N* HCl, and (*c*) sufficient H_2O to make 100 ml. Mix thoroughly by inversion; read a portion in a colorimeter (Bausch & Lomb Monochromatic 505-mμ filter) set at 100% transmission exactly 30 sec. after addition of the last reagent, against a blank

containing water instead of starch and saliva. For standards, 0·5 g of α-amylase is dissolved in sufficient 2% aq. NaCl soln. to yield a vol. of 10 ml. From this soln. are prepd. standards containing respectively 4, 3, 2 and 1 mg of α-amylase per 0·1 ml. Of 1228 specimens of saliva tested, 55% contained less than 1·5 mg of α-amylase per ml, only 5% more than 5 mg per ml. No correlation was found between amylase content, lactobacillus counts, acid production in selective media, or vol. of saliva. CHEM. ABSTR.

4099. **Colorimetric method for rapid determination of arginase activity.** D. D. Gilboe and J. N. Williams, jun. (Dept. Biochem., Univ. Wisconsin, Madison, U.S.A.). *Proc. Soc. Exp. Biol. Med.*, **1956**, **91** (4), 537–539.—The method depends on the incubation of a soln. of arginine at 37° with a liver homogenate in sodium pyrophosphate buffer at pH 9·5. After 10 min., 1 ml of the incubation mixture is added to 4 ml of 0·4% trichloroacetic acid. The unhydrolysed arginine is then determined by the Sakaguchi colorimetric method as modified by the authors (*Anal. Abstr.*, 1957, **4**, 4094). N. E.

4100. **Alteration of infra-red spectra of steroids in potassium bromide [discs].** G. Roberts (Sloan-Kettering Inst. for Cancer Res., New York, U.S.A.). *Anal. Chem.*, 1957, **29** (6), 911–916.—The quality and reproducibility of the spectra vary according to the dispersion of the steroid in the potassium bromide disc. Mixing by vibration in an agate ball-mill at 60 c.p.s. and hand grinding in a mullite mortar produce spectral differences. There is a smoothing-out of the spectrum and diminution or loss of some bands in the vibrated specimen; this change is discernible after vibration for about 3 min. and reaches a max. after about 15 min. More dilute specimens show greater deterioration than more concentrated ones. Reversion of the altered spectrum to that of the more normal one of the hand-ground disc can be achieved by heating the pressed disc at 100° to 110° for 5 min., hand-grinding and re-pressing. In the recommended procedure, 2 mg of steroid is vibrated with 400 mg of KBr for 15 min., then pressed at 7 tons per sq. in. for 3 min. The pellet is heated at 105° for at least 3 min. If it remains clear, the spectrum is determined. If it becomes opaque, it is hand-ground and re-pressed, and the new spectrum accepted. R. E. ESSERY

4101. **New paper-chromatographic system for the separation of polar corticosteroids.** W. J. Nowaczynski and E. Koiw (Hôtel-Dieu Hosp., Montreal, Quebec, Canada). *J. Lab. Clin. Med.*, 1957, **49** (5), 815–818.—The procedure described is more rapid than with Zaffaroni's propane-1:2-diol - toluene system and gives equally satisfactory separation. Whatman No. 2 paper (15 cm × 60 cm) is extracted with a mixture of benzene and methanol (1:1) in a Soxhlet apparatus for 72 hr. The dry paper is wetted before use with ethanediol - abs. methanol (1:1) and excess is removed by blotting. Development of 25 μg of corticosteroids is with toluene (50 ml) at 21° for 48 hr. No equilibration period is required. The compounds are detected under u.v. light and determined by u.v. absorption or with tetrazolium blue. Application of the system to the determination of urinary aldosterone is described. W. H. C. SHAW

See also Abstracts 4895, 3990, 3994, 4125, 4215.

Drugs

4102. **Complexometric titrations in pharmaceutical analysis. XVI. Semi-micro determination of narcotine, papaverine, codeine, strychnine and brucine.** B. Buděšínský (Res. Inst. Pharm. and Biochem., Prague, Czechoslovakia). *Českosl. Farm.*, 1956, **5** (10), 579–581.—Narcotine, papaverine, codeine, strychnine and brucine are pptd. from 0·5 *N* HCl with 0·028 *M* Bi - EDTA and 0·112 *M* KI forming iodobismuthate complexes in acid soln. and EDTA is set free. All five alkaloids react with the iodobismuthate forming compounds of the type $(B^{n+})_3[(BiI_4)^-]_{2n}\cdot(I^-)_n$. After centrifuging, the free EDTA is determined in an aliquot of the supernatant liquid by titration with 0·01 *M* $ZnSO_4$ in a borate buffer (pH 9·1) with Eriochrome black T as indicator. The determination is possible unless tertiary amines, quaternary ammonium salts or analogous sulphonium, phosphonium and arsonium compounds are present. J. VOLKE

4103. **Chromatographic separation of ergot alkaloids on impregnated paper.** P. Horák and S. Kudrnáč (Res. Inst. Med. Plants, Prague, Czechoslovakia). *Českosl. Farm.*, 1956, **5** (10), 595–596.—*Procedure*—Strips of Whatman No. 4 paper (50 cm) are impregnated with a mixture of 35 parts of formamide, 10 parts of urea and 5 parts of water, diluted, after the pH has been adjusted to 8·5 with aq. NH_3, with 50 parts of methanol. The chromatogram is developed with light petroleum - benzene (6:4) for about 6 hr. with the solvent overflowing. All water-insoluble ergot alkaloids can be separated in this way. J. VOLKE

4104. **The conductimetric determination of moisture in digitalis and ergot.** J. K. Wier and V. E. Tyler (Univ. Nebraska, Coll. Pharmacy, Lincoln, U.S.A.). *Drug Standards*, 1956, **24** (4), 117–121.—The Behlen Moisture Tester, Model A, is sufficiently accurate for routine determinations of moisture in digitalis and ergot. N. E.

4105. **A chromatographic - densitometric procedure for analysis of the solanaceous alkaloids.** T. J. Quinn, J. G. Jeffrey and W. C. MacAulay (Coll. of Pharm., Univ. Saskatchewan, Canada). *J. Amer. Pharm. Ass., Sci. Ed.*, 1957, **46** (6), 384–386.—A densitometric method has been applied to the determination of solanaceous alkaloids following paper-chromatographic separation. The results of the assays of several extracts of belladonna, hyoscyamus and stramonium agree with those by the B.P. method, but a large number ($\lesssim 10$) of replicates is needed for satisfactory precision. *Procedure*—Extract the alkaloids and dissolve in 0·1 *N* HCl to give a concn. of about 1%. Spot a 5-μl aliquot on to Whatman No. 1 paper and allow to dry. Develop for 7 hr. at 30° with a water-saturated mixture of butanol - acetic acid (20:1) and allow to dry. Dip into modified Dragendorff reagent, dry, and determine the max. extinction of the spot with a Welch densitometer, with a green filter. Calculate by reference to a standard curve. A. R. ROGERS

4106. **Comparative study of two methods of assay for reserpine.** W. A. Mannell and M. G. Allmark (Dept. Nat. Health & Welfare, Ottawa, Canada). *Drug Standards*, 1956, **24** (1), 6–10.—The methods of Sakal and Merrill (*cf. Anal. Abstr.*, 1955, **2**, 1005) and of Dechene (*cf. Anal. Abstr.*, 1956, **3**,

1477) were compared for the assay of reserpine in tablets. The former method based on u.v. absorption was unsuitable for some brands of tablets, but Dechene's method, based on fluorescence, was satisfactory. N. E.

4107. **Assay of artemisia.** N. A. Qazilbash (Islamia Coll., Peshawar, Pakistan). *Pakistan J. Sci. Res.*, 1956, **8**, 78–79.—Artemisia (15 g) is mixed with Na_2CO_3 (1·5 g), shaken with 15% aq. NH_3 (15 ml) then with 150 ml of benzene for 3 hr., left overnight and filtered. A 100-ml aliquot of the benzene extract is evaporated to dryness, dissolved by heating with 5% (w/v) $Ba(OH)_2$ soln. (100 ml), filtered, acidified and extracted with 25-, 20-, 15- and 10-ml portions of CCl_4. The combined extracts are evaporated, the residue is dissolved by boiling in 15% ethanol (50 ml), the filtrate purified with charcoal and kieselguhr, again filtered, and cooled. After 24 hr. the crystallised santonin is filtered off, dried and weighed. Corrections are made for santonin retained on the charcoal and dissolved in the filtrate (6·4 mg per 10 ml of filtrate). CHEM. ABSTR.

4108. **Gravimetric estimation of camphor via its semicarbazone.** K. K. Kaistha (State Drugs Control Lab., Punjab, Ambala Cantt, India). *Drug Standards*, 1956, **24** (4), 141–144.—The method has been modified for use in the determination of camphor in medicinal preparations containing essential oils. The separated oily fraction ($\equiv \simeq 0{\cdot}2$ g of camphor) in 80% aldehyde-free ethanol (5 ml), semicarbazide hydrochloride (2 g) and fused K acetate (1·5 g) were refluxed on a water bath for 3 hr. at 70°. Water (20 ml) was added, the mixture was stirred and cooled in ice, and the ppt. was filtered off and weighed. N. E.

4109. **Identification of amylobarbitone (Amytal) and pentobarbitone sodium (Nembutal) in mixtures.** E. G. Brooker (Dominion Lab., D.S.I.R., Wellington, New Zealand). *Analyst*, 1957, **82**, 448–449.—Unlike mixtures of most of the common barbiturates, amylobarbitone and pentobarbitone sodium in admixture are not readily separated by paper chromatography. Pentobarbitone sodium is readily dealkylated to 5-ethylbarbituric acid when heated with conc. H_2SO_4 for 1 hr. at 100°, whereas amylobarbitone is not affected. In the method described, the mixture is heated in this way, and the diluted product is continuously extracted with ether in a liquid - liquid extractor. The extract is dried with Na_2SO_4, then evaporated, and the residue is dissolved in chloroform (0·5 ml). Aliquots of this soln. (25 to 50 μl) are used for chromatography. The spots on the chromatogram are best located by the u.v. light fluorescent screen technique of Grieg (*Brit. Abstr. C*, 1953, 132). A. O. JONES

4110. **Reduction of iodomethanesulphonic acid by dropping mercury electrode. Polarographic method for the estimation of Urombral.** L. Fey. *Stud. Cercet. Chim., Cluj*, 1956, **7** (1–4), 69–76.—Experiments have shown that the $E_{\frac{1}{2}}$ for iodomethanesulphonic acid is a function of pH between pH 0·42 and 4·75. The supposition that this is due to simultaneous processes, namely that at the lower pH the non-dissociated acid is reduced, and at the higher pH the anion itself is reduced, is deduced from first principles and confirmed by experiment. Optimum conditions for the polarographic determination of Urombral have been established. H. SHER

4111. **Polarographic titrations of organic bases. IV. Complex mercury compounds and Reinecke salt as volumetric reagents.** M. Čiháková and J. Zýka (Inst. Anal. Chem., Charles' Univ., Prague, Czechoslovakia). *Československ. Farm.*, 1956, **5** (10), 572–577.—Soln. of K_2HgI_4, K_2HgBr_4 and $K_2Hg(SCN)_4$ were investigated as reagents for polarographic titration of organic bases (alkaloids). For practical titration the soln. of K_2HgI_4 containing an excess of iodide is most suitable. The titration is carried out with a dropping mercury electrode, at the potential $-0{\cdot}8$ V to $-0{\cdot}9$ V (*vs.* the S.C.E.) with 0·1 *M* KNO_3 or 0·1 *M* H_2SO_4 as supporting electrolyte. Cinchonine and narcotine hydrochloride were thus determined. Reinecke salt (**I**) gives an anodic wave (corresponding to the thiocyanate constituent), and a cathodic wave with $E_{\frac{1}{2}}$ approx. $-0{\cdot}9$ V (corresponding to the reduction of the Cr^{III} complex). A third wave has not yet been completely explained. The titrations were performed at $-1{\cdot}2$ V in 0·1 *M* H_2SO_4 with 0·04 *M* **I**. The results are satisfactory for analytical purposes in only some cases, but in all instances the ratio of base to reagent in the ppt. was determined. J. VOLKE

4112. **Polarographic determination of Arfonad "Roche" [trimetaphan (+)-camphorsulphonate].** J. Kráčmar (State Inst. Control Drugs, Prague, Czechoslovakia). *Československ. Farm.*, 1956, **5** (10), 578–579.—Trimetaphan (+)-camphorsulphonate (**I**) reacts at pH 5·0 to 7·5 with picric acid forming an insoluble crystalline monopicrate. A polarographic titration of **I** is carried out with 0·01 *M* picric acid as reagent. After each addition the soln. is stirred for 5 to 8 min. until it is completely clear. A buffer soln. (Britton and Robinson) is used as supporting electrolyte, the current is read at $-0{\cdot}04$ V (*vs.* the S.C.E.). The mean error is $\pm$ 1 % for 25 to 50 mg of **I** in 15 to 25 ml. J. VOLKE

4113. **Application of flame photometry to analysis of medicaments. III. Determination of calcium.** J. Dorche and C. Costet (with J. Lux). *Ann. Pharm. Franç.*, 1956, **14** (11), 669–677.—The effect on the reliability of determinations of Ca of the presence of other cations, of anions and org. substances and of the use of different flame-photometric techniques was investigated and it was found that the determination of Ca is more susceptible to error than that of the alkali metals. The interference from other ions is less when a hot flame (oxy-acetylene) is used instead of air - butane or air - coal-gas flames. The most useful emission line is that at 423 mμ. The analysis of several medicaments for Ca has shown that the standards must contain similar concn. of interfering substances. It is concluded that the method might be of some use for frequent determinations for control of a single medicament. E. J. H. BIRCH

See also Abstracts 4051, 4143, 4146, 4147, 4148.

Food

4114. **Trace elements in food. I. Lead.** R. D. A. Polhill. *Food Manuf.*, 1956, **31**, 182–184.—Various methods for the determination of Pb in foods are given. N. E.

4115. **Colour evaluation in the cane-sugar industry.** V. R. Deitz. *J. Res. Nat. Bur. Stand.*, 1956, **57** (3), 159–170.—A single numerical measure of the colour of sugar solutions is defined as the NBS unit. It is shown that the colours of sugar solutions are confined in a narrow band of a chromaticity plot and that the log of the "attenuancy" (A), which $= -\log_{10}$ [transmittance of solution/transmittance of solvent], and therefore takes into account scattering, bears within limits a linear relation to log λ, and this line can be defined by two observations (at 420 and 560 mμ). The spectrophotometric data are converted to Munsell value functions (V) and the difference in NBS units from a reference standard of purified sucrose is given by —

$$\Delta E_{NBS} = 50\sqrt{[0{\cdot}23(10-V_y)]^2+[V_x-V_y]^2+[0{\cdot}4\,(V_z-V_y)]^2}.$$

A chart is given from which ΔE_{NBS} can be read off by entering A at 420 and 560 mμ. This unit of colour difference is shown to correlate better with visual estimation than earlier methods. A formula for calculating the colour of mixtures from the value of the components is given and discussed.

E. J. H. Birch

4116. **New reagent for estimation of reducing sugars.** K. S. G. Doss, S. C. Sen and J. P. Bansal. *Sugar*, 1957, **52** (6), 33.—The use of a copper reagent incorporating EDTA (disodium salt) instead of a Fehling type of reagent has been investigated. The reagent consists of an aq. soln. of 9 g of EDTA (disodium salt), 5 g of NaOH and 3·5 g of $CuSO_4.5H_2O$ in 100 ml of water.

Sugar Ind. Abstr.

4117. **Determination of starch in starch-containing materials by amperometric titration.** J. Holló and J. Szejtli (Tech. Univ., Budapest). *Stärke*, 1956, **8** (5), 123–125.—A modification of the technique of Coton *et al.* (*J. Sci. Food Agric.*, 1955, **6**, 660) is described, based on the quant. fixation of iodine by starch. A starchy solution behaves as a non-conductor and additions of iodine have virtually no effect on the conductivity until the whole of the starch present has been used up and there is free iodine present. The conductivity then begins to rise, being proportional to the concn. of free iodine. The quantity of starch can thus be deduced from the amount of iodine used up before the conductivity has begun to rise. Consistently accurate results and speedy operation (about six parallel determinations per hour) are claimed.

A. Tessler

4118. **Estimation of protein in wheat and flour by ion-binding.** D. C. Udy (Agric. Exp. Sta., Pullman, Washington, U.S.A.). *Cereal Chem.*, 1956, **33** (3), 190–197.—The protein of wheat and flour can be estimated by a method that depends on the power of the protein to bind a fixed proportion of the dye, Orange G. The method is applicable to samples having a wide range of protein content. *Procedure*—Prepare a soln. of the dye to contain 0·1 g of pure Orange G in 100 ml of a soln. buffered to pH 2·2 [citric acid (20·7 g) and Na_2HPO_4 (1·44 g) per litre]. Add the sample (0·6 g of flour or 0·5 g of wheat, finely ground in a Weber pulverising mill) to a 50-ml polyethylene centrifuge tube, followed by 25 ml of the dye soln. Close the tube, and shake (15 min. for flour, or 4 hr. for wheat) and finally centrifuge at 4000 r.p.m. to obtain a clear liquor. Determine the extinction of the supernatant soln. in a special 0·2-mm cell, with a 470-mμ filter in an Evelyn absorptiometer. From the results, calculate the amount of bound dye and find the protein content from a curve obtained by plotting the bound dye (mg per g of flour) against the protein determined by the Kjeldahl method.

D. G. Forbes

4119. **Cryoscopy of milk: a 1954-1956 survey. I. Distribution of freezing-points among 1627 herd milks. II. Tests on replicate samples. III. Freezing-point trends *versus* environmental and herd-management conditions.** A. H. Robertson (New York State Dept. Agric. and Markets, Albany, N.Y., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1957, **40** (2), 618–628; 628–632; 632–660.—Observations were based on 1627 inspector-authenticated herd samples. The average f.p. was — 0·543°; only 29·6% of the samples had f.p. of — 0·550° or lower. If the 3% water tolerance is strictly applied to this average, 2·0% of the genuine samples would be deemed adulterated; if the same tolerance is applied to the official average (— 0·550°), 12·2% would be so deemed. Because of area differences in f.p., complete justice requires reference to the area average f.p. Collaborative results are reported and compared. The f.p. of milk is not altered by a pasteurisation - homogenisation treatment or by sterilisation in a sealed can. Of the 49 variables in environmental or herd-management conditions studied, 11 factors may cause f.p. to be lower than the average, and 19 factors may cause f.p. to be higher than the average.

A. A. Eldridge

4120. **Examination of dried milk.** L. S. Malowan (Biochem. Lab., Univ., Panama). *Milchwissenschaft*, 1956, **11**, 468–469.—By a reaction of ketoses, previously described (*Biochim. Biophys. Acta*, 1948, **2**, 95; 1950, **5**, 147), sucrose added to dried milk is readily detected. After casein has been removed from the reconstituted milk by adding conc. HCl and centrifuging, 100 mg of 3-methylindole in 5 ml of HCl is added to 2 ml of the milk serum; fructose formed from sucrose gives an immediate blue colour, extractable with $CHCl_3$; glucose does so only slowly, and galactose and mannose not at all.

Nutr. Abstr. Rev.

4121. **Simple colorimetric determination of milk proteins.** R. Schober and H. F. Hetzel (Staatl. Milchw. Lehr- und Forschungsanstalt, Wangen i.A., Germany). *Milchwissenschaft*, 1956, **11** (4), 123–126.—To a soln. (10 ml) of diluted milk or whey (1; 15), Amido black (Bayer) (0·6165 g per litre) in citrate - phosphate buffer (17·28 g of citric acid and 2·375 g of $Na_2HPO_4.2H_2O$ per litre) or citrate - phthalate buffer (11·85 g of citric acid and 7·85 g of K H phthalate per litre) was added at pH 2·8. The resulting colour was measured on a Zeiss spectrophotometer at 578 mμ. Inorganic salts from lactic acid or lactose did not interfere under these conditions.

D. P. Felix

4122. **The separation of milk proteins by means of column chromatography.** R. Schober and H. F. Hetzel (Staatl. Milchw. Lehr- und Forschungsanstalt, Wangen i.A., Germany). *Milchwissenschaft*, 1956, **11** (2), 63–65.—The protein complex is first adsorbed on Al_2O_3 (pH 4·2) and the individual proteins are subsequently separated by elution with citrate and phosphate buffers. The pH of the Al_2O_3 column must be kept constant; the same precaution applies to the concn. of the buffer

eluents. After separation, the proteins were determined spectrophotometrically by means of the biuret reaction. This method gave results comparing satisfactorily with the usual electrophoresis procedure, and it was possible to differentiate between the protein composition of untreated and heat-treated varieties of milk. A. TESSLER

4123. **Rapid method for the determination of lactose in milk and cheese.** A. J. G. Barnett and G. Abdel Tawab (Dept. Biol. Chem., Chem. Buildings, Old Aberdeen, Scotland). *J. Sci. Food Agric.*, 1957, **8** (7), 437–441.—Phenol - H_2SO_4 reagent can be used for the colorimetric determination of sugars, and details of the procedure with lactose as a reference are described for the estimation of this compound in milk and cheese samples. The sugar can be detected in concn. of < 50 μg per ml, and the method is readily applicable to the study of variations in the lactose content during the souring of milk and the ripening of cheese. Interference by other substances normally present is negligible, and 95 to 100% recovery is claimed. *Procedure*—In a series of absorptiometer tubes place measured vol. (0 to 2 ml) of a standard soln. of lactose (0·05 g per litre), and dilute each vol. to 2 ml. Add 6 drops of uniform size of a soln. of phenol (80 g in 20 ml of H_2O) to each tube, followed by 5 ml of conc. H_2SO_4. Measure the colours produced with the use of a blue filter against a reagent blank, and prepare a standard curve. Prepare a soln. of the sample by diluting milk (1 g) to 1 litre with water or, with cheese, by grinding 1 g with H_2O (6 × 10 ml) in a mortar, and diluting the mixed extracts to 1 litre. Filter the soln. through two thicknesses of paper (Whatman No. 42), reject the first 10 ml of filtrate, and then treat 2 ml of the clear filtrate with the reagents as before. Calculate the lactose content of the sample by reference to the standard curve. D. G. FORBES

4124. **Detection of refined lard and refined "white grease."** J. Wurziger. *Fette, Seif., Anstrichmitt.*, 1957, **59** (2), 90–93.—The presence in lard of $\not<$ 10% of refined "white grease" or refined inferior lard is indicated by positive results in all three of the following tests—(*i*) neutral-red fluorescence (Schönberg, *Fleisch- und Milchhyg.*, 1942/43, **53**, 61, 91); (*ii*) aniline point - iodine number (APIN) (van Voorst, *Chem. Weekbl.*, 1951, **47**, 333); and (*iii*) cholesterol determination. In the fluorescence test, lard that has been treated intensively with bleaching-earth shows a white background tint, and refined offal fat a chalky-white background tint; in order to prevent masking of these colours by the colour change of the neutral red, the samples are first treated with a soln. of aq. NH_3 (0·5%). The APIN is determined from—

APIN = 3·12 (aniline point + 0·32 × acid value + 0·06 × Lea no.) + iodine number.

Genuine lard invariably gives APIN values $\not<$ 162. It also usually contains $\not>$ 0·01% of cholesterol, but the cholesterol content of adulterated lard can sometimes be reduced to this figure by intensive treatment with bleaching-earth. E. HAYES

4125. **Spectrophotometric semi-micro determination of ergosterol in yeast.** O. N. Breivik and J. L. Owades (Fleischmann Lab., Standard Brands, Inc., Stamford, Conn., U.S.A.). *J. Agric. Food Chem.*, 1957, **5** (5), 360–363.—The method described is applicable to samples containing 5 to 100 mg of yeast solids and 0·05 to 2·0 mg of "ergosterols." The yeast is digested with ethanolic KOH and ergosterols are extracted with a measured vol. of *n*-heptane. A portion (1 ml) of the heptane soln. is diluted with abs. ethanol (10 ml) and the extinction is determined at 281·5 and 230 mμ. The total "ergosterols" content is calculated from the value at 281·5 mμ and that of 24(28)-dehydroergosterol from the value at 230 mμ. The difference between these two findings gives the percentage of ergosterol. S.C.I. ABSTR.

4126. **Rapid method of hop analysis.** J. O. Harris (Newcastle Breweries, Ltd., Newcastle-upon-Tyne). *J. Inst. Brewing*, 1956, **62** (6), 468–469.—The ground hops (10 g) are extracted in a Soxhlet apparatus with light petroleum (b.p. $< 40°$) for 30 min. The solvent is removed completely under reduced pressure and the residue is triturated with pure methanol (75 ml), allowed to stand for 15 min., filtered into a 100-ml flask and made up to vol. with methanol. An aliquot is evaporated to constant wt. for total sol. resin. A second aliquot (15 ml) is allowed to percolate under slightly reduced pressure through a column of decolorising charcoal (0·1 g) supported on a 10-mm sintered glass funnel which has a total capacity of 20 ml. The charcoal is washed with 8 ml of methanol and the combined eluate and washings are made up to 25 ml with methanol. The "humulone" content is determined polarimetrically in a 2-dm tube, assuming $[\alpha]_D$ for α-acids to be $-$ 206·24°. Comparative analyses by this method and that of Ford and Tait (*J. Inst. Brewing*, 1932, **38**, 351) show substantial agreement. The present method is suitable for rapid routine analysis for control of hop-rates. R. E. ESSERY

4127. **Estimation of reducing sugars. Electrolytic estimation of copper separated as cuprous oxide from Fehling's solution. Application to wines and preserved foods.** P. Klantschnigg (Staz. Sper. Olivicolt., Pescara, Italy). *Ann. Sper. Agr.*, 1956, **10**, 1405–1415.—Reducing sugars were estimated by the iodimetric method of Intonti (*Ann. Chim. Appl., Roma*, 1930, **20**, 583) and by a gravimetric method in which the Cu of the cuprous oxide from Fehling's soln. is estimated electrolytically. The results obtained by electrolysis were in general slightly below, while those obtained by the iodimetric method were slightly above, the theoretical value. The procedure for applying the electrolytic method to wines and preserved foods is described. NUTR. ABSTR. REV.

4128. **Polarographic determination of heavy metals in wines.** J. Bonastre and R. Pointeau (Sta. Oenolog. et Agronom. de Bordeaux, France). *Chim. Anal.*, 1957, **39** (5), 193–196.—A detailed description is given of a method for the polarographic determination of Pb, Zn, Cu and Mn in samples of wine. Zinc is determined by a method similar to that of Stout *et al.* (*Coll. Czech. Chem. Commun.*, 1938, **10**, 129), which involves ignition, extraction from an alkaline citrate buffer with a soln. of dithizone in $CHCl_3$, re-extraction into 0·5 *N* HCl and polarography in a supporting electrolyte of NH_4SCN - ammonium acetate - acetic acid; $E_{\frac{1}{2}}$ for Zn is $-$1·06 V (*vs.* the S.C.E.). The method for Pb is the same; $E_{\frac{1}{2}} = -0·46$ V. Copper is not removed from the organic layer in the extraction with 0·5 *N* HCl and is finally determined by polarography in 0·06 *N* EDTA at pH 8; $E_{\frac{1}{2}} = -0·40$ V. Manganese is determined by polarography of an

extract of the ignited material in a supporting electrolyte of KCN - ammonium citrate - aq. NH_3; $E_{\frac{1}{2}} = -1{\cdot}36$ V. A micro-cell suitable for polarography of 2-ml samples is described.

A. R. ROGERS

4129. **The *in situ* determination of iron and of copper in wine.** W. M. Banick and G. F. Smith (Univ. of Illinois, Urbana, U.S.A.). *Anal. Chim. Acta*, 1957, **16** (5), 464–472.—Iron and Cu are determined in wine without ashing of the samples. *Iron in red wine*—Mix 5 ml of wine with 5 ml of acetic acid - Na acetate buffer soln. (pH 4·0), 2 ml of 10% hydroxylamine hydrochloride soln., 1 ml of 0·01 *M* 4:7-diphenyl-1:10-phenanthroline in ethanol and 2 ml of 95% ethanol. Boil the soln. for 1 min., transfer while still hot to a separator and shake with 6 ml of *iso*amyl alcohol for 30 sec. Discard the aq. layer. Rinse the beaker with 1 ml of 95% ethanol and two 5-ml portions of water and add the rinsings to the separator. Add 10 ml of buffer soln. (pH 4·0), and shake for 30 sec. Separate the alcoholic phase, dilute to 10 ml with 95% ethanol and determine the extinction at 533 mμ by comparison with a reference liquid obtained by extracting 5 ml of the sample with 6 ml of *iso*amyl alcohol and diluting the extract to 10 ml with 95% ethanol. *Iron in white wine*—Proceed as for red wine but omit the ethanol from the initial mixture; cool after boiling and add the rinsings to the separator before extracting with *iso*amyl alcohol. *Copper in red and white wines*—Mix a 5-ml sample with 5 ml of buffer soln. (pH 4·0), 0·2 ml of $CuSO_4$ soln. (1 ml ≡ 0·1277 mg of Cu), 2 ml of 10% hydroxylamine hydrochloride soln., 2 ml of 0·01 *M* 2:9-dimethyl-4:7-diphenyl-1:10-phenanthroline in ethanol and 6 ml of *iso*amyl alcohol. Shake for 2 min. and discard the aq. layer. To the alcoholic soln. add 5 ml of ammonium acetate buffer (pH 7·1), and shake for 1 min. Separate the alcoholic layer, dilute to 10 ml with 95% ethanol and determine the extinction at 479 mμ with a reference liquid prepared as described for Fe. Results for both Fe and Cu are in good agreement with those obtained with 1:10-phenanthroline and 2:9-dimethyl-4:7-diphenyl-1:10-phenanthroline, respectively, after wet-ashing with HNO_3 and $HClO_4$.

W. C. JOHNSON

4130. **Determination of added distinctive cations in whisky. VIII. Flame-spectrophotometric determination of magnesium.** M. J. Pro and R. A. Nelson (Alcohol and Tobacco Tax Div. Lab., Internal Revenue Service, Washington, D.C., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1957, **40** (2), 575–582.—The procedure for the flame-photometric determination of Mg, added to whisky as a brand marker, involves the determination of emission intensities (at 382 mμ) of soln. of the sample ash with dextrose (to minimise interference by phosphate and sulphate), of a background standard containing dextrose, Na and K, and of a simulated Mg standard also containing dextrose, Na and K. The use of standard background and simulated Mg standards is necessary because Na and K, present in whisky, enhance the emission due to Mg. The presence of more than 4 p.p.m. of Fe causes interference. For 1 to 3 p.p.m. of Mg, the method gives satisfactory results.

A. A. ELDRIDGE

4131. **The bisulphite determination of free and combined aldehydes in distilled spirits.** J. F. Guymon and J. A. Nakagiri (Dept. Viticulture and Enology, Univ. of California, Davis, U.S.A.). *J. Ass. Off. Agric. Chem.*, 1957, **40** (2), 561–575.—The indirect procedure, whereby excess of bisulphite is added to the solution containing aldehyde, and the unchanged portion is determined by titration with iodine, gives a measure of free aldehyde together with such amount of aldehyde as may have been released by partial hydrolysis of the acetal present. In the direct method, the excess of bisulphite is destroyed by iodine at a pH which does not permit the aldehyde - bisulphite compound to dissociate; the compound is then hydrolysed and the released sulphite is titrated with iodine. The direct method is applied to the determination of total and free aldehyde in brandy; the procedure is described.

A. A. ELDRIDGE

4132. **A paper-chromatographic method for the analysis of food colourings.** I. Netto (Lab. Centr. de Normalizacao et Fiscalizacao de Produtos, Lisbon, Portugal). *Ann. Falsif.*, 1957, **50**, 166–173.—The method described is for the rapid detection of those colourings that are permitted by the Portuguese authorities for use in foods. They comprise Ponceau 3 R, amaranth, Naphthol yellow S, tartrazine, Guinea green B and indigotin. *Procedure*—The chromatogram is run with *N* HCl at 17° to 23° by the downward technique until the solvent front has progressed for 35 cm. The paper is removed and allowed to dry. The red colours, indigotin and tartrazine have the lowest R_F values and are visible in white light; Naphthol yellow S is seen under u.v. light, at a distance of 24 cm from the starting line; and Guinea green B is rendered visible at the foot of the paper after exposing it to the action of NH_3 vapour.

D. G. FORBES

4133. **Trace elements in edible fats. IV. Separation and spectrophotometric determination of zinc.** A. Vioque and M. del Pilar Villagrán (Inst. de la Grasa, Seville, Spain). *Grasas y Aceites*, 1956, **7** (5), 239–242.—The sample is ashed at 450° in the presence of $Mg(NO_3)_2$, the ash is dissolved in 6 *N* HCl, Cu and Fe are removed, and the Zn is extracted with $CHCl_3$ as the diethyldithiocarbamate. The Zn^{2+} are then liberated with 0·05 *N* HCl and determined spectrophotometrically with dithizone. A few milligrams of Zn (in the presence of Fe and Cu) may be determined to within ± 15%.

L. A. O'NEILL

4134. **A semi-quantitative method for the determination of NN′-diphenyl-*p*-phenylenediamine (DPPD) in chicken fat and eggs.** W. Pudelkiewicz, L. M. Potter, L. D. Matterson and E. P. Singsen (Univ. Connecticut, Storrs, Conn., U.S.A.). *Poultry Sci.*, 1956, **35**, 959–960.—DPPD was detected in depot fat and in eggs by extraction in the cold (− 20° F) with acetone and development of a red colour with conc. HNO_3, which is read at a wavelength of 520 mμ. DPPD was detected in egg yolk and depot fat from hens fed as little as 0·0125% in the diet.

CHEM. ABSTR.

4135. **Determination of 2:6-di-*tert.*-butyl-*p*-cresol in edible fats by ultra-violet spectrophotometry.** M. A. Phillips and R. D. Hinkel (Koppers Co., Inc., Verona, Pa., U.S.A.). *J. Agric. Food Chem.*, 1957, **5** (5), 379–384.—A method is described for determining 2:6-di-*tert.*-butyl-*p*-cresol (**I**) (0·002 to 0·2%), when used as an antioxidant in lard, in

the presence of other allowable preservatives, including butylated hydroxyanisole, nordihydroguaiaretic acid, propyl gallate, citric acid, mono*iso*propyl citrate and H_3PO_4. The sample of lard dissolved in *cyclo*hexane (10 ml) is passed through a chromatographic column packed with 100-mesh silicic acid. The **I** is selectively removed with successive portions of *cyclo*hexane passed through the column; the filtrates are collected in six 50-ml fractions and the extinction is measured at 284 mμ. Analyses of five different commercial lards gave recoveries within the range 99 ± 3%, and from other samples recoveries were consistently > 93%.
S.C.I. Abstr.

4136. **The application of u.v. spectrophotometry to the examination of the quality of fatty foods.** J. P. Wolff. *Ann. Falsif.*, 1957, **50**, 149–162.—Measurement of the u.v. absorption can be applied to the estimation of antioxidants in oils and fats. The standard absorption due to the pure oil or fat at the selected wavelengths must be known. For a sample containing gallic acid esters or butylated hydroxyanisole, the oil (25 ml) dissolved in *cyclo*hexane (25 ml) is extracted with ethanol (4 × 25 ml) at 72°, and the extinction of the mixed extracts is measured at 285, 274 and 242 mμ. By substitution of the values obtained in equations specific for each oil, the proportion of one or more of the antioxidants can be calculated. For the estimation of dibutoxytoluene, the unsaponifiable matter is used and, after preliminary concentration by chromatography, this compound can be determined by spectrophotometric methods.
D. G. Forbes

4137. **Spectrophotometry in analysis of oils and fats.** N. H. E. Ahlers (Unicam Instruments Ltd., Cambridge). *Paint Technol.*, 1956, **20**, 237–241, 277–283, 324–328, 357–360, 401–404; 1957, **21**, 6–8, 13.—The applications of u.v. and i.r. spectrophotometry to the study of the composition of oils and fats and their geometrical isomerism, the determination of component fatty acids, and the examination and analysis of oxidised, polymerised and copolymerised oil products are reviewed. The determination of trace metals by visible spectrophotometry and flame photometry, the u.v. spectroscopy of the rosin acids and the possibilities of Raman spectroscopy in oil analysis are also considered.
L. A. O'Neill

4138. **Spectrophotometric determination of the degree of unsaturation of oils.** J. Moretti. *Peint.-Pigm.-Vern.*, 1957, **33** (2), 133–135.—The proposed method, which is quantitative, consists in alkaline isomerisation of the mixture to form conjugate double-bonds, thus giving a higher u.v. absorption. Absorption spectrum curves give several peaks, one less than the number of double bonds. The absorption coeff. for acids of 2 to 6 double bonds are known, and from the given data the nature and concentration of each fatty acid can be calculated. The method is not recommended for a mixture of unknown composition, but rather as a means of checking the progress of an oxidation or polymerisation reaction.
F. J. M.

4139. **The Bellier method [for arachis oil].** A. Ibarra (La Plata Univ., Argentina). *Ann. Ass. Quim. Brasil.*, 1953 [1956], **12** (3), 151–155.—The original Bellier method (1899) is shown to be more convenient than some later modifications. A table is given showing turbidity points and percentages of sunflower, cottonseed, turnip-seed, and peanut oils in olive oil mixtures. In a test-tube (20 cm × 3 cm) saponify 1 ml of oil with 5 ml of ethanolic KOH (8%), neutralise to phenolphthalein with aq. acetic acid (1:2), add 50 ml of ethanol (70°) warmed in the same bath, and 3 drops of HCl (sp. gr. = 1·06). Allow to cool slowly with gentle agitation and note temperature of turbidity. By addition of 9 drops of HCl (sp. gr. = 1·06) results are concordant with those obtained by the modified Bellier method in which glacial acetic acid is added after neutralisation.
G. F. Penny

4140. **Spectrophotometric estimation of chlorophyll and pheophytin in olive oil.** M. Mingot Lorenzo. *An. Inst. Nac. Invest. Agron., Madrid*, 1956, **5**, 295–307.—The absorption of chlorophylls *a* and *b* and pheophytins *a* and *b* are given at 2·5-mμ intervals from 600 to 700 mμ. The solutions obey Beer's law.
L. G. L. Unstead-Joss

4141. **Determination of lipoperoxides.** B. Coleby (Low Temp. Sta., Univ. of Cambridge). *Chem. & Ind.*, 1957, (33), 1123–1124.—During investigations into the $Fe(SCN)_3$ method of colorimetry for the determination of peroxides in autoxidised lipids, it was found that the claims of Glavind and Hartmann (*cf. Anal. Abstr.*, 1955, **2**, 2558) that increasing the concn. of the NH_4SCN reagent to 6% eliminated interference by phospholipids were only partly substantiated, the time required to develop full colour was very variable, and the yield in no case agreed with the stoicheiometric expectation. It is therefore considered that the application of this method to oxidised fats gives results of doubtful value.
J. F. P. H. Greene

4142. **The peroxide test in static and dynamic fat analysis.** K. Täufel (Humboldt Univ., Berlin). *Fette, Seif., Anstrichmitt.*, 1957, **59** (2), 87–90.—For the rapid determination of peroxide values, a soln. of fat in dil. acetone is treated with a soln. of $FeSO_4$ and NH_4SCN, and the colour of the $Fe(SCN)_3$ produced is compared with permanent standards. *Procedure*—A stock soln. of reagent is prepared by dissolving 5 g of $FeSO_4.7H_2O$ in 50 ml of 10% NH_4SCN containing 0·5 ml of conc. H_2SO_4; 0·7 g of iron powder is added and the flask is closed by a Bunsen valve. The test reagent is prepared by filtering 2·5 ml of this soln. into a mixture of 12·5 ml of acetone and 12·5 ml of freshly dist. de-aerated water. Weighed samples of fat (0·025 and 0·05 g for fats having peroxide values of from 2 to 10, calculated as ml of 0·002 *N* $Na_2S_2O_3$ per g of fat) are dissolved in acetone and the soln. are made up to 10 ml; 0·2 ml of reagent is added to each soln., which is then set aside for 5 min. The colours produced are compared with standards prepared by diluting various aliquots of a 30% soln. of $Co(NO_3)_2.6H_2O$ to 50 ml with a mixture of methanol and water (5:1) containing 10% v/v of conc. HCl. The standards are calibrated by comparison with colours produced with oils of known peroxide value; these reference values are determined by the method of Sully (*Anal. Abstr.*, 1954, **1**, 977). The colorimetric method gives results in good agreement with those obtained by the latter method.
E. Hayes

4143. **Physicochemical determination of vitamin D.** Katsutoshi Miwa (Hokkaido Regional Fisheries Res. Lab., Yoichi). *Vitamins, Japan*, 1955, **9**, 399–403.—Optimum conditions were found for

determining vitamin D (**I**) in fish-liver oils of very low **I** potency. The use of a bull-neck-like chromatographic column (1·5 cm in diam. and 6 cm high) instead of a thin column was found to be suitable for this purpose. Chromatography of **I** could be performed with a combination of activated alumina and acetone - light petroleum (1:9). The recoveries were 99 ± 7%. The **I** potency of pollack-liver oil (about 3000 i.u. per g) was determined by this method within the confidence limits of 13·2%.
CHEM. ABSTR.

4144. **The determination of vitamin B_1 [thiamine] in cereal products.** A. Wilmes. *Bull. Éc. Meun. Belg.*, 1955, **17** (1), 10–13, (3), 52–63; 1956, **17** (5), 91–95, (6), 110–113; **18** (1), 9–16; 1957, **18** (6), 124–133.—This series of papers covers an investigation of published methods; the author gives his preference as (*i*), for white flour, the A.A.C.C. No. 1 method; (*ii*) for bran, weatings, complete flour and other products containing thiamine as cocarboxylase and interfering substances, the S.P.A. chemical method with some modifications. N. E.

4145. **Circular paper chromatography. X. Separation, identification and quantitative estimation of riboflavine and flavin compounds.** K. V. Giri and P. R. Krishnaswamy (Dept. of Biochem. Indian Inst. of Sci., Bangalore). *J. Indian Inst. Sci.*, 1956, **38** (4), 232–244.—Micro quantities of riboflavine and derivatives (flavin mononucleotide, flavin-adenine dinucleotide, lumiflavin and lumichrome) may be separated more readily by circular rather than vertical paper chromatography. The best solvent system was found to be *n*-butanol - acetic acid - water (4:1:5), with the procedure as previously reported (*Nature*, 1952, **169**, 923). The bands are visualised by u.v. light and estimated by fluorescence after elution with water. R_F values of the compounds in the order given above, on Whatman No. 1 paper, are—0·45, 0·29, 0·17, 0·52 and 0·69. The use of the method in studying riboflavine metabolism in a mutant yeast BY2 is described. D. G. LLOYD

4146. **Polarographic determination of riboflavine.** G. P. Tikhomirova, A. M. Shkodin and A. I. Ermakova (Ukr. Training and Res. Inst. Food Ind., Kharkov). *Ukrain. Khim. Zhur.*, 1956, **22**, 687–690.—Determinations were made of riboflavine dissolved in 0·1 *N* KCl, Clark and Lubs buffer (pH 7·8) and Kolthoff buffer (pH 8·6). In all cases there was a linear relation between the concn. of riboflavine and the height of the wave. Also, as the pH increased, the $E_{\frac{1}{2}}$ rose. Of the tested electrolytes, the Kolthoff buffer gave the best results. To determine riboflavine, first obtain a polarogram of the test soln. and then a polarogram of a mixture of 9 ml of test soln. and 1 ml of standard soln. The results are calculated by a formula for the method of addition. CHEM. ABSTR.

4147. **Paper chromatography of tocopherols.** A. Kopecký (Výzk. ústav. oleje a tuky, Usti n. L., Czechoslovakia). *Průmysl Potravin*, 1956, **7**, 267–269.—A method is described for the qual. detection of α-, γ- and δ-tocopherols in soya-bean oil and pharmaceutical prep. with aq. methanol on paper impregnated with 20% of petroleum oil and $AgNO_3$ as detecting agent. CHEM. ABSTR.

4148. **Determination of (±)-α-tocopherol acetate (vitamin E).** K. Pietroniuk (Inst. of Pharmaceutics, Warsaw). *Chem. Anal., Warsaw*, 1957, **2** (1), 77–91.—The method depends on measuring the extinction at 480 mμ of the red colour formed with fuming HNO_3. K. F. SPOREK

4149. **Note on elytral patterns of storage insects.** R. F. Heuermann (Food and Drug Admin., Dept. of Health, Education and Welfare, Washington, D.C., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1957, **40** (2), 661–664.—Some elytral pattern characteristics (*cf.* Heuermann and Kurtz, *Anal. Abstr.*, 1956, **3**, 854) require time for development. Elytral patterns of ageing insects (1 to 33 days) were examined and the development of characteristic markings is described and illustrated for *Tribolium confusum*. A. A. ELDRIDGE

See also Abstracts 4001, 4002, 4024, 4050.

Sanitation

4150. **Flame-photometric determination of alkal and alkaline-earth elements in waters. I. Sodium and potassium.** Ken Sugawara, Tadashiro Koyama and Nobuko Kawasaki (Fac. Sci., Univ. Nagoya, Japan). *Bull. Chem. Soc. Japan*, 1956, **29** (6), 679–683.—The addition of many alcohols, aldehydes, ketones and surface-active compounds increases the intensity of emission of Na and K in the flame photometer. This is the basis of a sensitive (0·1 p.p.m.) method for the determination of Na and K in natural waters. *Procedure*—Mix the sample (40 ml) with acetone (2·5 ml), butyl alcohol (2·5 ml) and 5% aq. laurylamine hydrochloride (2·5 ml). Dilute with H_2O to 50 ml and measure the intensities flame-photometrically. Large amounts of Ca (20 p.p.m.) or Mg (25 p.p.m.) cause an error of − 2% for Na and − 1% for K.

II. Calcium and strontium. Ken Sugawara, Tadashiro Koyama and Nobuko Kawasaki. *Ibid.*, 1956, **29** (6), 683–685.—Organic acids, especially tartaric acid, increase the intensities of emission in the flame-photometric determination of Ca and Sr, although acetone and butyl alcohol and similar solvents have little effect. The emission due to Sr increases uniformly with increase in concn. of Ca. Magnesium interferes to a marked extent and must be removed. *Procedure*—For Ca, evaporate the sample of natural water (< 500 ml) to 100 ml, add aq. HCl (1:1) (2 ml), saturated ammonium oxalate soln. (20 ml), urea (10 g) and methyl red soln. (2 drops) and warm until the colour changes to orange - yellow. Dissolve in dil. HCl, filter, add 20% tartaric acid soln. (2·5 ml) to the filtrate, dilute to 50 ml and measure the intensity at 560 mμ in the flame photometer. For Sr, treat the sample (< 2 litres) in the same way with the addition of a suitable known amount of $CaCl_2$ soln. and measure at 460·7 mμ. Calculate with the aid of a calibration curve. A. R. ROGERS

4151. **A modified palmitate method for the estimation of total hardness of water.** W. G. Macmillan and M. C. Mitra (Indian Jute Mills Ass. Res. Inst., Calcutta). *J. Indian Chem. Soc., Ind. Ed.*, 1956, **19**, 182–184.—The water under test is made alkaline and then titrated directly with K or Na palmitate soln., with Eriochrome black T as

indicator. The method is simple, reproducible and of sufficient accuracy for use in rapid routine analysis. I. JONES

4152. **Determination of the nitrate ion in water.** R. Müller and O. Widemann. *Vom Wasser*, 1955, **22**, 247–271.—Oxidation methods (diphenylamine - sulphuric acid and brucine - sulphuric acid) were found to be much inferior to nitration methods (sodium salicylate and phenoldisulphonic acid) for operation with a photometric apparatus. The sodium salicylate method is preferred as being less sensitive to interfering factors.
WATER POLLUTION ABSTR.

4153. **Spectrophotometric micro-determination of arsenic in natural waters and its application to silicate and biological materials.** Ken Sugawara, Motoharu Tanaka and Satoru Kanamori (Fac. Sci., Univ. Nagoya, Japan). *Bull. Chem. Soc. Japan*, 1956, **29** (6), 670–673.—By this method, 2 μg of As in 3 litres of water can be determined with an error of $\pm$ 5%. Interference is caused by 1-mg quantities of most heavy metals and by much larger quantities of P, Si, Fe, Al, Mn and Ti. *Procedure*—Warm the sample of water, or an appropriate extract of silicate or biological material, to 70° or 80° with $FeCl_3$ soln. in a porcelain beaker. Add excess of aq. NH_3, cool and filter. Digest the filter-paper and ppt. with HNO_3 (2 ml) and H_2SO_4 (5 ml) for 1 to 3 hr., adding more HNO_3 in small portions to avoid carbonisation. Transfer to a quartz dish and remove the excess of HNO_3 by gentle heating. Dilute with water (25 ml), warm, add 25% aq. KI (2 ml), cool and remove the liberated iodine with $Na_2S_2O_3$ soln. Shake twice with 0·1% K xanthate soln. (5 ml) and CCl_4 (3 ml). To the combined CCl_4 layers add 10% H_2SO_4 (1·2 ml), water (2 ml) and sufficient Br - CCl_4 (1:25) to give a deep-red colour. Shake. Wash the CCl_4 layer with water (3 ml). Wash the combined acid and water extracts with CCl_4 (2 $\times$ 3 ml), add 2% ammonium molybdate soln. (0·4 ml) and 0·1% hydrazine sulphate soln. (0·4 ml) and dilute to 10 ml with water. Heat in boiling water for 30 min., cool, and measure the extinction at 840 mμ. A. R. ROGERS

4154. **Quantitative determination of fluoride in phosphate-bearing waters.** B. G. Lang, O. C. Sieverding and E. K. Borman. *Amer. J. Publ. Hlth*, 1956, **46**, 860–864.—The method depends upon addition of sufficient thorium nitrate to provide an excess after reaction with fluoride. Determination of unbound Th is accomplished spectrophotometrically at 595 mμ with chromazurol-S as indicator, with the use of a standard curve. WATER POLLUTION ABSTR.

4155. **Identification of anionic synthetic detergents in foams and surface waters.** A. A. Rosen, F. M. Middleton and N. W. Taylor (Robert A. Taft San. Eng. Center, USPHS, Cincinnati, Ohio, U.S.A.). *J. Amer. Wat. Wks Ass.*, 1956, **48** (10), 1321–1330.—Anionic detergents in liquefied foam are extracted by passage through a column of activated carbon. The carbon is extracted successively with $CHCl_3$ and 95% ethanol. This treatment removes only part of the detergent, thus making the method useless for quant. work. The extracted detergents are then examined by i.r. spectroscopy. To detect traces of anionic detergent in tap or surface water, a complexing agent (cetyltrimethylammonium bromide) is added to the alcohol extract of the carbon. The complex may then be extracted with $CHCl_3$, providing a separation from other organic contaminants of the water sample.
G. S. ROBERTS

4156. **The amount of beryllium in sea water.** Masayoshi Ishibashi, Tsunenobu Shigematsu and Yasuharu Nishikawa (Ishibashi Lab.). *Bull. Inst. Chem. Res., Kyoto Univ.*, 1956, **34** (4), 210–213 (in English).—To a sample of artificial sea water containing a known quantity of Be were added $FeCl_3$ and HCl, followed by aq. NH_3, dropwise. The ppt., after being set aside overnight, was filtered off, dried, and ignited, and the residue treated with ice water and filtered. Potassium cyanide, to inhibit interference from Zn, and ethanolic morin soln. were added, and the yellowish fluorescence was measured with a fluorophotometer. Recovery of added Be was 86%. Two samples of sea water examined by this method contained 0·03 and 0·4 μg of Be per litre, respectively. F. J. M.

4157. **Recommended methods for the analysis of trade effluents. Methods for the determination of aluminium and zinc.** The Joint A.B.C.M. - S.A.C. Committee on Methods for the Analysis of Trade Effluents. *Analyst*, 1957, **82**, 443–448.—For both metals the test soln. is that resulting from removal of organic matter by wet oxidation. For Al, the sample soln. (up to 20 μg of Al) is mixed with $FeCl_3$ ($\equiv$ 1 μg of Fe), dil. thioglycollic acid and with aq. NH_3 until the colour just changes to violet and then with 2 ml of 5 *N* HCl, 3 ml of starch soln. (1%), 5 ml of ammonium acetate soln. and, after dilution to 45 ml, 3 ml of 0·2% aq. aluminon soln. After adjustment to 50 ml the liquid is heated in boiling water for 4 min., allowed to cool slowly during 1 hr. and then maintained at 20° $\pm$ 0·5° for 30 min. The colour is measured spectrophotometrically at 520 mμ or absorptiometrically or visually. For amounts of Zn $>$ 5 mg per litre, the test soln. is extracted at pH 5·5 with a chloroform soln. of dithizone, Zn (with Bi and Cd) is extracted from the chloroform phase with dil. HCl and, after evaporation, the Zn is treated with KI in the presence of $K_3Fe(CN)_6$ and the liberated iodine is titrated with thiosulphate. For contents of Zn up to 5 mg per litre, Cu is removed, if necessary, and Zn is separated from other metals by extraction with dithizone at pH 4·7. Excess of dithizone is removed by Na_2S, and the Zn dithizonate in CCl_4 soln. is determined spectrophotometrically at 532 mμ. A. O. JONES

4158. **Simple method of estimating oxygen value of wastes.** N. Porges, L. Jasewicz and S. R. Hoover. *Ind. Wastes*, 1956, **1**, 95–98.—Conc. H_2SO_4 containing 0·0125 *N* $K_2Cr_2O_7$ is the oxidising agent and complete reduction of the $K_2Cr_2O_7$ is detected by means of the indicator ferrous *o*-phenanthroline.
WATER POLLUTION ABSTR.

4159. **Estimation of sulphonic acids in the presence of sulphuric acid. Application to the analysis of acid sludge.** V. Cerchez and O. Popescu. *Stud. Cercet. Chim., Cluj*, 1956, **7** (1–4), 155–165.—The sulphonic acids together with H_2SO_4 are pptd. as barium salts. Assuming that the mean mol. wt. of the sulphonic acids is known, the difference between the wt. of the barium salts dried and calcined enables the amount of H_2SO_4 present to be calculated. The use of nitrobenzene and water for fractionation of acid sludges is recommended.
H. SHER

4160. **Analytical determination of trace constituents in metal-finishing effluents. XII. The determination of orthophosphates in effluents.** E. J. Serfass and R. F. Muraca (Lehigh Univ., Bethlehem, Pa., U.S.A.). *Plating*, 1956, **43**, 356–358.—The method is the standard one of the APHA modified to eliminate F^-, As, silica and highly coloured substances. The sample is heated to fuming with HNO_3 and H_2SO_4, reduced with KI, and repeatedly evaporated with HCl. Insoluble substances are filtered off, ammonium molybdophosphate is pptd. and filtered off, then redissolved, repptd., reduced to molybdenum blue, and the colour intensity measured.

XIII. The volumetric determination of sulphate in effluents. E. J. Serfass and R. F. Muraca. *Ibid.*, 1956, **43**, 500–501.—The sample is pptd. with OH^- and Ag^+ to remove interfering ions; F^- are removed by evaporation with HCl, and organic material is oxidised with H_2O_2. The SO_4^{2-} are then titrated with $BaCl_2$, with tetrahydroxy-*p*-benzoquinone as indicator. The method is useful in the 5 to 50 p.p.m. range.

XV. The colorimetric determination of cyanates in effluents. D. G. Gardner, R. F. Muraca and E. J. Serfass. *Ibid.*, 1956, **43**, 743–746.—Ammonium salts are removed by boiling with excess of alkali hydroxide in the presence of alkali sulphide. Cyanate is then hydrolysed to NH_4^+ by boiling in acid soln., and determined colorimetrically with Nessler reagent. The sensitivity is 5 p.p.m. and the limit of detection is 1 p.p.m.

XVI. The colorimetric determination of total and free cyanides. E. J. Serfass and R. F. Muraca. *Ibid.*, 1956, **43**, 1027–1030.—For obtaining total CN^-, the sample is heated under reflux with dilute H_2SO_4 and $CuCl_2$. Liberated HCN is collected in NaOH and converted into CNCl with chloramine T. The CNCl reacts with pyridine in the presence of 3-methyl-1-phenyl-5-pyrazolone to form a deep-blue colour, the intensity of which is measured. For obtaining free CN^-, the sample is heated under reflux with dil. acetic acid. The sensitivity is 0·1 p.p.m. and the limit of detection is 0·02 p.p.m.

CHEM. ABSTR.

See also Abstracts 3888, 3956, 4022, 4208.

Agriculture and Plant Biochemistry

4161. **Determination of magnesium in plant ash.** P. M. Ashwin and J. A. Ritchie (Dominion Lab., Wellington, N.Z.). *N.Z. J. Sci. Tech., B*, 1957, **38** (5), 447–450.—In the determination of Mg in plant ash, interfering Fe is masked by CN^-, and Al by triethanolamine. *Procedure: standardisation of EDTA*—To soln. containing a known amount of Mg add two drops of methyl red, triethanolamine soln. (25% v/v) (1 ml) and ammonium oxalate soln. (3% w/v) (5 ml). Heat on a steam bath adding conc. aq. NH_3 dropwise until the last drop changes the colour to yellow; digest for a further 5 min.; cool. Place the beaker in crushed ice; add buffer soln. [NH_4Cl (30 g) and conc. aq. NH_3 (285 ml) diluted to 500 ml] (4 ml), 10 drops of KCN soln. (10% w/v) and a crystal of hydroxylamine hydrochloride; cool thoroughly. Add 6 to 10 drops of Solochrome black (0·25 w/v) and run in the EDTA (disodium salt) soln. (approx. 2 g per litre), with stirring, until the colour changes to grey; then stir well and continue the titration, dropwise, until a well-developed green colour appears

Preparation of sample soln.—Weigh 1 g of the oven-dried sample, ash overnight at 430°, cool and weigh. Transfer the ash to a 30-ml beaker, add 10 drops of HNO_3, 1 ml of H_2SO_4 and 5 drops of 72% $HClO_4$. Evaporate to fuming, cool, dilute with water and filter. Dilute to 100 ml. Transfer a 25-ml aliquot and complete the determination as for the standardisation of EDTA, the titration being made in the presence of pptd. Ca oxalate. The method is accurate to ±1%.

H. B. HEATH

4162. **Polarographic and amperometric determination of calcium in sugar-beet juices by means of complexones. I, II.** K. Číž and V. Valter. *Listy Cukr.*, 1956, **72**, 55–57; 85–87.—The Buriánek and Durdík polarographic method for hardness was simplified, and CaO estimated from a graph. Amperometric titration was carried out with 1 ml of 0·5% gelatin soln., 2 ml of the unknown soln., 3 ml of 0·1 *M* $Zn(NO_3)_2$, and 4 ml of conc. aq. NH_3, and with calomel and dropping mercury electrodes. The titrant was 0·01 *M* EDTA (disodium salt) which was added at the rate of 2 drops per sec. at a potential of − 1·5 V. In amounts less than 0·0025 *M*, Cu, Mg, Al and Fe did not interfere. The results were accurate and the method was suitable for the determination of Ca in all intermediate and final products. The titration soln. were prepared by adding to 2 ml of sugar juice, or other intermediate, 1 ml of 0·5% gelatin soln., 3 ml of 0·1 *M* EDTA (zinc salt) and 10 ml of conc. aq. NH_3. The soln. was titrated at − 0·8 to − 1·6 V. For the amperometric determination the same amounts of soln. as above were taken, 3 ml of 0·01 *M* $Zn(NO_3)_2$ was added and the soln. was titrated at − 1·5 V with 0·01 *M* EDTA (disodium salt) by using calomel and dropping mercury electrodes at the rate of less than 2 drops per sec. The higher values of the polarographic method were found to be due to the presence of Mg, but the amperometric method gave accurate results and was particularly suitable for coloured soln.

CHEM. ABSTR.

4163. **Rapid procedure for the chromatographic separation and spectrophotometric estimation of certain pasture lipids. I. Carotene, xanthophyll and chlorophyll.** N. A. Worker (Massey Agric. Coll., Palmerston North, New Zealand). *J. Sci. Food Agric.*, 1957, **8** (7), 442–444.—The simple method described for the separation of carotene (**I**), xanthophyll (**II**) and chlorophyll (**III**) from samples of dried or fresh grass avoids the necessity for preliminary saponification. Spectrophotometric determination following isolation of the compounds gave 97 to 100% recovery. *Procedure*—Prepare a chromatographic column, 3 cm high, with Al_2O_3 (Brockmann, grade 3) in light petroleum containing ethanol (8%). Strengthen the top of the column with 1 ml of light petroleum. Grind dried grass (1 g) or fresh grass (5 g) to pass a 0·5-mm sieve, moisten with a few drops of water, and extract in an atmosphere of N with acetone (60 ml) for 5 min. Filter off the acetone and repeat the extraction, first with 60 ml, then with 25 ml, of acetone. Dilute the mixed filtrates to 150 ml. Dry 3 ml of the soln. on a water bath at 60° and dissolve the residue in 3 ml of light petroleum for chromatography. Transfer this soln. to the column, and elute with a soln. of acetone in light petroleum (2%), which removes **I**. Further elute with a soln. (25 ml) of ethanol in light petroleum (1%), which removes **III**, and finally with a soln. (25 ml) of

ethanol in light petroleum (8%) to elute **II**. **I** and **II** are determined in the eluates from measurements of the extinctions of the soln. at 451 mμ and 441 mμ, respectively. For **III**, measurements are made at 664 and 645 mμ, allowance being made for variation in the ratio of chlorophyll-*a* to chlorophyll-*b*. D. G. FORBES

4164. **A method of evaluating chlorophyll in plants.** M. Mingot Lorenzo. *An. Inst. Nac. Invest. Agron., Madrid*, 1956, **5**, 261–294.—The methods of the A.O.A.C., 1945, 140, and MacKinney (*J. Biol. Chem.*, 1941, **140**, 315) are compared. An alternative method proposed is to extract three times 5 to 10 g of leaf (together with a little $CaCO_3$ or Na_2CO_3) with anhydrous acetone in a mill, filtering each extract, and making the combined extracts to a known vol., usually 500 to 1000 ml. The extract is diluted to a known vol. with water so that 80% v/v acetone is obtained. The extinction of the solution is measured in a Beckman DU spectrophotometer at 630 and 645 mμ. The absorption coeff. of MacKinney are used to calculate the results. L. G. L. UNSTEAD-JOSS

4165. **Determination of zinc in plants and soils.** E. T. Verdier, W. J. A. Steyn and D. J. Eve (Rhodes Univ., Grahamstown, S. Africa). *J. Agric. Food Chem.*, 1957, **5** (5), 354–360.—The dithizone and polarographic methods were critically examined and a modified procedure, based on the dithizone photometric method of Cowling and Miller (*Ind. Eng. Chem., Anal. Ed.*, 1941, **13**, 145) is described. The influence of pH on the extraction of Zn, transmittance curves, and accuracy were studied. The speed of analysis was increased and 24 determinations per day were made, giving accurate and precise results. All measurements were made at 520 mμ. A modified polarographic method is described which could be applied to the simultaneous determination of Cu, Ni, Mn and even Co, although the presence of phosphate might interfere with the determination of Mn. S.C.I. ABSTR.

4166. **Determination of fluorides in plant tissue, air and water. Apparatus and procedures.** J. Gwirtsman, R. Mavrodineanu and R. R. Coe (Boyce Thompson Inst. for Plant Res. Inc., Yonkers, N.Y., U.S.A.). *Anal. Chem.*, 1957, **29** (6), 887–892.—Tissue is ignited and the residue fused with NaOH. The F is isolated as H_2SiF_6 by steam-distillation of the cake with SiO_2 and $HClO_4$ in the presence of Ag^+. The F^- in the distillate is determined by direct or back-titration with standard Th^{4+} at pH 3 with alizarin red S as indicator; the end-point is identified visually or spectrophotometrically. Fluoride in air or water is determined similarly, after absorption or concentration. The calibration curve is linear up to 300 μg of F^- and blank titrations are low. Practically all interferences are said to be eliminated by the procedures which are given in great detail. Steam-distillation, absorption and spectrophotometric titration apparatus is described in full. D. A. PANTONY

4167. **Detection of free amino acids in soil.** T. M. B. Payne, J. W. Rouatt and H. Katznelson. *Soil Sci.*, 1956, **82**, 521–524.—Soil samples (3 kg) are leached with successive portions of water, each portion being sufficient to saturate the soil and remaining in contact with the soil for 1 hr. before being allowed to drain. The combined leachate (1 litre) is concentrated by freeze-drying and free amino acids in the concentrate are detected chromatographically, a procedure inapplicable if the leachate is concentrated at moderate temperatures, *e.g.*, *in vacuo* at 40°. A. G. POLLARD

4168. **Determination of available phosphorus in tropical soils by extraction with sodium hydroxide.** D. H. Saunder (Min. Agric., S. Rhodesia). *Soil Sci.*, 1956, **82**, 457–463.—The soil sample (2 g) is leached on filter-paper with 25 ml of *N* NaCl containing HCl (0·1 *N*) to remove exchangeable Ca. Calcareous soils are further treated with HCl to remove chalk. The residual soil and paper after draining are digested with 100 ml of 0·1 *N* NaOH on a water bath for 1 hr., loss of water being minimised by a Bunsen valve. Sodium chloride (0·5 g) is added to the suspension (to aid flocculation), which is then filtered. A 15-ml aliquot of the filtrate (first runnings are discarded) is acidified with 4 ml of *N* HCl and diluted to 25 ml. After 1 hr., pptd. organic matter is removed by filtration, and phosphate is determined in the filtrate. A. G. POLLARD

4169. **A spectrochemical analytical procedure for the determination of trace elements in soils, fertilisers and biological materials.** K. Scharrer and G. K. Judel (Agrikulturchem. Inst., Justus-Leibig-Hochschule, Giessen). *Z. anal. Chem.*, 1957, **156** (5), 340–352.—Traces of Ag, Cu, Mn, Mo, Pb, V and Zn can be determined. Fertilisers may be extracted with water or mineral acid; wet-ashing is used for soils and biological samples. Separation and concn. of the trace elements from these soln. are described. All the required elements are estimated at one setting of the spectrograph, with Fe and Cd as internal standards. Iron must be estimated in the sample first; Cd does not occur in these materials and must be added. Standard deviations are reported for each element. G. BURGER

4170. **Spectrophotometry in the analysis of soils and tobacco plants. I. Methods for determining sodium, potassium and calcium in tobacco leaves.** J. Oliver and J. A. Galbis (Inst. de Biologia del Tabaco, Seville, Spain). *Bol. Inst. Invest. Agron., Madrid*, 1956, **16**, 255–293.—The three ions were estimated by using a Beckman DU spectrophotometer with flame attachment, and their influence on one another was studied. The Na present raises the apparent content of Ca by 2 to 4% if 2·5 to 10 p.p.m. of Na is present with 25 to 200 p.p.m. of Ca, and raises the apparent content of K of solutions containing 25 to 200 p.p.m. of K by about 1%. L. G. L. UNSTEAD-JOSS

4171. **Determination of phosphorus in fertilisers by automatic titration.** J. A. Brabson and W. D. Wilhide (Div. of Chem. Development, T.V.A., Wilson Dam, Ala., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1957, **40** (2), 594–606.—The pH of the end-point in the titration of ammonium molybdophosphate by the official (A.O.A.C.) method with the use of phenolphthalein, and by the method involving addition of formaldehyde (*cf.* Shuey, *Anal. Abstr.*, 1956, **3**, 586) was determined. The phenolphthalein end-point comes after the equivalence point in the official method and before the equivalence point when formaldehyde is added. Excess of formaldehyde suppresses the hydrolysis of Na_2HPO_4, thereby lowering the pH of the

equivalence point. The procedure for automatic titration, with a Sargent - Malmstadt titrator (Malmstadt and Fett, *Anal. Chem.*, 1954, **26**, 1348; 1955, **27**, 1757; Sargent Co., *Sci. Apparatus and Methods*, 1955, **7**, 2), of ammonium molybdophosphate pptd. by the A.O.A.C. method, and with formaldehyde as a complexing agent for the NH_3, is described. Results obtained by the automatic method were more accurate than those afforded by the A.O.A.C. volumetric method.

A. A. ELDRIDGE

4172. **Determination of organic acids in silage.** H. G. Wiseman and H. M. Irvin (Dairy Husbandry Res. Branch, U.S. Dept. of Agric., Beltsville, Md., U.S.A.). *J. Agric. Food Chem.*, 1957, **5** (3), 213–215.—Lactic and succinic acids are widely separated by the partition chromatographic method described. The silage extracts are prepared with 0·6 *N* H_2SO_4 and chromatographed on a Celite column containing Alphamine red R as an internal indicator and conc. sucrose soln. as stationary phase. The individual silage acids are eluted with successive mixtures of acetone and Skellysolve B in various proportions and the eluates are titrated with alkali. The single-zone collection of eluates reduces the no. of titrations to a minimum with increase in accuracy. Average recoveries of 97·5 to 101% were obtained with single acids and 95 to 105% for individual acids in a mixture containing formic, acetic, propionic, butyric, lactic and succinic acids.

S. C. JOLLY

4173. **Modifications of pepsin-digestibility method for animal proteins.** A. J. Gehrt, M. J. Caldwell and W. P. Elmslie (Moorman Mfg. Co., Quincy, Ill., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1957, **40** (2), 606–617.—A collaborative study of methods for determining the relative digestibility of feeding-stuffs employed the Moorman method (*cf.* Gehrt *et al.*, *Anal. Abstr.*, 1955, **2**, 1963), the Moorman method with incubation at 50° for 16 hr. instead of at 37° for 40 hr., and the American Meat Institute method involving incubation at 52° for 7 hr. Variations of results are discussed. Protein digestibility is sharply decreased by overcooking. The optimum pH for pepsin digestion is $\simeq$ 1·5. The accelerated methods require continuous automatic agitation.

A. A. ELDRIDGE

4174. **Improved determination of chromic oxide in cow feed and faeces.** F. T. Kimura and V. L. Miller (Western Washington Exp. Sta., State Coll. of Washington, Puyallup, U.S.A.). *J. Agric. Food Chem.*, 1957, **5** (3), 216.—A rapid and specific colorimetric method is described for the determination of Cr_2O_3 in feed and faeces in amounts commonly used as indicator in digestibility trials with dairy cattle. The standard deviation was $\pm$ 0·018 mg in the range 0·3 to 0·8% of Cr_2O_3. *Procedure*—The sample (1 g), containing 3 to 7 mg of Cr_2O_3, is boiled gently with HNO_3 (10 ml) and sodium molybdate (1 to 5 mg) until approx. half of the acid is evaporated ($<$ 10 min.). After cooling slightly, 70% $HClO_4$ (5 ml) is added to the mixture, and the oxidation is completed in 10 to 15 min. by boiling more vigorously and then heating for a further 2 to 3 min. The mixture is allowed to cool to room temp., diluted to 100 ml with water, centrifuged or allowed to stand for the SiO_2 to settle, and the colour of the soln. is measured photometrically with a 440-mμ filter. The amount of Cr_2O_3 is determined by reference to a standard curve prepared by measuring the colour of standard soln. of $K_2Cr_2O_7$ of approx. the same acidity as the test soln. and containing the equiv. of 10 to 80 μg of Cr_2O_3 per ml.

S. C. JOLLY

4175. **Nutritive value of *Calluna vulgaris*. IV. Digestibility trials. [Determination of nitrogen in faeces.]** A. N. Smith and B. Thomas (King's Coll., Univ. Durham). *J. Agric. Sci.*, 1956, **47**, 468–475.—In digestibility trials with sheep a one-tenth aliquot of the wet faeces from each animal daily was dried for 48 hr. at 35° to 38°. At the end of the 10-day trial period, the dried samples were bulked and milled, 2-g samples being taken from the bulk for the determination of N. Results thus obtained did not differ significantly from those yielded by the customary daily analysis of wet samples.

A. G. POLLARD

4176. **Determination of ethylene dibromide in fumigated fruit.** B. H. Kennett and F. E. Huelin (Div. of Food Preservation, C.S.I.R.O., Homebush, N.S.W., Australia). *J. Agric. Food Chem.*, 1957, **5** (3), 201–203.—The sample of fumigated fruit (100 to 150 g) is boiled for 90 min. with 100 ml of water and 10 ml of benzene in a flask fitted with a special reflux head in which the benzene collects and extracts the ethylene dibromide from the condensate before the condensate is returned to the flask. The separated benzene extract is mixed with 2 ml of benzene used for washing the condenser and reflux head, and the mixture is boiled under reflux for 15 min. with 25 ml of ethanol and 1 ml of 2 *N* NaOH. The solvents are then removed and the residue is heated over a Bunsen flame until no further decrepitation occurs and the residue, which may be slightly charred, is dry. To the cooled residue, 20 ml of water is added, followed by 10 ml of $Na_2HPO_4.2H_2O$ soln. (20% w/v) and 5 ml of NaOCl soln. (10% w/v), the mixture is heated to boiling and 5 ml of Na formate soln. (50% w/v) is added. After cooling to room temp., 1 ml of KI soln. (25% w/v), one drop of ammonium molybdate soln. (5% w/v) and 10 ml of 9 *N* H_2SO_4 are added in succession, and the liberated iodine is titrated with 0·005 *N* $Na_2S_2O_3$ to starch soln. (x ml). A blank titre (y ml) is obtained by treating 20 ml of water, 1 ml of 2 *N* NaOH, 10 ml of the Na_2HPO_4 soln. and 5 ml of the NaOCl soln. as in the determination. The wt., in mg, of ethylene dibromide = 31·31 $\times$ 0·005 $\times$ ($x - y$). Recoveries of 99 to 101% were obtained when 0·5 to 15 mg of ethylene dibromide in benzene soln. was added to samples of fruit.

S. C. JOLLY

4177. **Determination of small amounts of total organic chlorine in solvent extracts of vegetable material.** Analytical Methods Committee of the Society for Analytical Chemistry. *Analyst*, 1957, **82**, 378–382.—Report of the Pesticides Residues in Foodstuffs Sub-Committee. The test material was a soln. in light petroleum of the residue obtained by evaporation of the benzene extract of uncontaminated green cabbage. This soln. was freed from Cl^- by washing with water, a known amount of DDT was added and colouring matter was removed by chromatography on alumina with a light petroleum - benzene eluent. After removal of the eluent, the residue was boiled under reflux with *iso*propyl alcohol and Na for 30 min., aq. *iso*propyl alcohol was then added and boiling was continued until the Na had disappeared. The

slightly acidified soln. was extracted with ether, the aq. layer was treated with H_2O_2 to remove sulphides and made slightly alkaline to phenolphthalein. An aliquot was almost neutralised with H_2SO_4, evaporated to dryness, the aq. soln. of the residue was slightly acidified, concentrated (5 ml), made just alkaline to a screened methyl red indicator and titrated to a faint violet-grey with 0·002 *N* H_2SO_4. Mercuric oxycyanide reagent (prep. described) was added and the liquid was titrated to the original colour with 0·002 *N* H_2SO_4. After a blank correction the content of Cl was found by calculation. Standardisation of the H_2SO_4 with respect to Cl, an alternative procedure for the application of the mercuric oxycyanide method, and a method for preparing Cl-free Na are described.

A. O. JONES

4178. **Determination of organic chlorides and residues from chlorinated pesticides by combustion analysis.** J. A. Hudy and C. L. Dunn (Research Center, Hercules Powder Co., Wilmington, Del., U.S.A.). *J. Agric. Food Chem.*, 1957, **5** (5), 351–354.—The apparatus comprising a vertical, quartz-packed furnace is described. Liquid org. materials may be burnt continuously at rates of 10 to 20 g per hr. The chloride resulting from combustion is determined by amperometric titration with $AgNO_3$ after absorption in alkaline soln. In application of the method to toxaphene (chlorinated camphene, 67 to 69% of Cl) in various materials, *e.g.*, animal fat and butter fat, a sensitivity of 5 μg of chloride was found.

S.C.I. ABSTR.

4179. **Chemical determination of Perthane residues on agricultural crops.** J. R. W. Miles (Canada Dept. Agric., Chatham, Ontario). *J. Agric. Food Chem.*, 1957, **5** (5), 349–350.—Perthane [1:1-dichloro-2:2-di-(*p*-ethylphenyl)ethane] residues are extracted from the material with chloroform (1 ml per 2 g), the extract is dried with Na_2SO_4 and filtered. An aliquot portion is evaporated to dryness, 15 ml of a 1% ethanolic soln. of KOH is added, the tube is heated in a boiling-water bath until only 0·5 ml of the soln. remains (20 to 25 min.), cooled, light petroleum (25 ml) is added, the tube is stoppered, shaken for 3 min., Na_2SO_4 (3 g) and decolorising mixture ("Methods of Analysis", A.O.A.C., 8th Ed., 1955, p. 407) (1 g) are added and the tube is shaken for 2 min. After the mixture settles, the light-petroleum extract (15 ml) is transferred to a dry test-tube (in a bath at 35° to 40°) and the solvent is completely removed. Conc. H_2SO_4 (96%) (5 ml) is added and the colour is allowed to develop for 15 min. The extinction is measured at 493 mμ. Residues as low as 0·1 p.p.m. can be determined on asparagus and maize.

S.C.I. ABSTR.

4180. **Infra-red determination of *p*-chlorobenzyl *p*-chlorophenyl sulphide and its oxidation to its sulphone on pears.** F. A. Gunther, R. C. Blinn and M. M. Barnes (Univ. of Calif. Citrus Exp. Sta., Riverside, U.S.A.). *J. Agric. Food Chem.*, 1957, **5** (3), 198–201.—A chromatographic method is described for the separation of *p*-chlorobenzyl *p*-chlorophenyl sulphide (chlorbenside), its sulphoxide and its sulphone from extraneous pear extractives in light petroleum soln. by selective adsorption on an Attaclay-Hyflo Super-Cel mixture. The sulphide and sulphone are selectively eluted with light petroleum and benzene, respectively, while the sulphoxide remains strongly adsorbed. The amounts of the sulphide and sulphone in the eluates are determined from their i.r. absorption at 1094 and 1155 cm^{-1}, respectively.

S. C. JOLLY

4181. **The analysis of technical chlorbenside [*p*-chlorobenzyl *p*-chlorophenyl sulphide] and fluorbenside [*p*-chlorobenzyl *p*-fluorophenyl sulphide].** D. J. Higgons and W. H. Stephenson (Lenton Exp. Sta., Boots Pure Drug Co. Ltd., Nottingham, England). *Analyst*, 1957, **82**, 435–442.—The determination of *p*-chlorobenzyl *p*-chlorophenyl sulphide in the acaricide chlorbenside and *p*-chlorobenzyl *p*-fluorophenyl sulphide in fluorbenside is based on oxidation of the isomeric sulphides in glacial acetic acid with H_2O_2 to the corresponding mixture of the isomeric sulphones. The mixture is pptd. with alkali and the mixed sulphide content is calculated from the wt. of the ppt. To determine the *p*-*p*-sulphide content, the m.p. of the pure sulphone and of the sulphone obtained as described are determined and the proportion of *p*-*p*-sulphide is found from the difference by means of a eutectic m.p. graph. Total isomeric sulphides may also be determined by oxidation to sulphoxide with Br and, after addition of KI and acid, titration of the liberated iodine. To determine the biologically undesirable impurity bis-*p*-chlorophenyl disulphide (**I**) (in chlorbenside only), the sample is treated with ethanolic H_2SO_4, glacial acetic acid and zinc amalgam at 70° for 1 hr. The chlorbenside that has crystallised out is removed, and the filtrate is titrated with 0·05 *N* iodine. From the iodine absorption the content of **I** is calculated. For application of the H_2O_2 oxidation method to powders and the solid matter from liquid formulations, the active matter is extracted with acetone.

A. O. JONES

4182. **Enzymatic method for estimation of Sarin in dilute aqueous solution.** J. Epstein, M. Demek and V. C. Wolff, jun. (Chemical Corps Res. & Devel. Command, Army Chemical Center, Md., U.S.A.). *Anal. Chem.*, 1957, **29** (7), 1050–1053.—Concn. of 0·1 to 0·5 p.p.m. of Sarin (*iso*propyl methylphosphonofluoridate) are measured by the inhibiting activity on the hydrolysis of 2-phenylazo-1-naphthyl acetate by the esterases of horse serum to form the deep-red 2-phenylazo-1-naphthol. The standard esterase soln. is prepared from normal horse serum, and the substrate from 1:2-naphthaquinone. Vol. of 0 to 5 ml of standard aq. Sarin (0·5 p.p.m.) are made up to 5 ml with water in stoppered tubes, and to each are added 0·1 ml of esterase soln. and 0·1 ml of a prescribed phosphate buffer (pH 7·4 to 7·8). After mixing, the tubes are heated for 30 min. at 25°, 0·5 ml of substrate soln. (6×10^{-4} *M* in acetone) is added and the tubes are reheated for 10 min. After addition of 0·3 ml of acid acetone (0·5 *M* HCl-acetone) (1:2) the colour is measured and results are plotted. Replicate readings show coefficients of variation not exceeding 4·5%. No interference was found when using water containing 460 p.p.m. of alkali and alkaline-earth salts, or 250 p.p.m. of NaCl, or Fe^{3+} (2 p.p.m.) and Cu^{2+} (10 p.p.m.). Suggestions are made for improving the sensitivity in specific determinations.

R. E. ESSERY

4183. **Biochemical evaluation of paper chromatograms of parathion, its isomers and analogues.** K.-B. Augustinsson and G. Jonsson (Inst. of Org. Chem. and Biochem., Univ., Stockholm). *Acta Chem. Scand.*, 1957, **11** (2), 275–282 (in English).—Filter-paper (Munktell OB) was impregnated with

silicone (MS 550) from a 5% soln. in hexane and air-dried. Phosphate esters in ethanol soln. were applied, the paper was dried and developed by ascending chromatography with the upper phase of a H_2O - ethanol - $CHCl_3$ mixture (6:10:10). After air-drying, the paper was sprayed with 5% ethanolic KOH and exposed to steam, when the components became visible as yellow spots. For the biochemical evaluation, unsprayed chromatograms were cut into strips, usually 20, between starting line and solvent front, each section was extracted with bicarbonate buffer and the cholinesterase inhibition of the extracts was measured (Augustinsson, *Methods of Biochem. Anal.*, 1957, **5**, 1). R_F values at 22° and I_{50} values (molar concn. giving 50% inhibition) at 25° are tabulated for 12 known compounds and 3 unknowns obtained from a heated parathion prep. Both parathion and methylparathion, when applied to paper and stored, undergo changes to more active inhibitors, and enzyme inhibition should be tested immediately after chromatographic separation. Highly active inhibitors are also obtained on heating pure parathion in a sealed tube at 140° for 4 hr. The toxicity of commercial prep. of parathion depends largely on the presence of isomers that are formed spontaneously under various conditions and are difficult to assay chemically. This technique should be used to test the homogeneity of prep. that have been stored under uncontrolled conditions.

R. E. ESSERY

See also Abstracts 4025, 4045, 4134.

5.—GENERAL TECHNIQUE AND LABORATORY APPARATUS

General

4184. **Critical comparison of collection efficiencies of commonly used aerosol-sampling devices.** C. Schadt and R. D. Cadle (Stanford Res. Inst., Menlo Park, Calif., U.S.A.). *Anal. Chem.*, 1957, **29** (6), 864–868.—The performance of aerosol-sampling devices with different aerosols under different conditions is described. The devices used are—thermal precipitator, jet impactor, Greenburg-Smith impinger, electrostatic precipitator, membrane filter and sedimentation box. Marked discrepancies are often observed between theoretical and observed efficiencies, and possible reasons for this are discussed. K. A. PROCTOR

4185. **Automatic recording balance.** P. D. Gran (Bell Telephone Lab., Inc., Murray, N.J., U.S.A.). *Anal. Chem.*, 1957, **29** (5), 839–841.—An electronically controlled null-point instrument, designed for thermogravimetric and related uses, is described; a linear variable differential transformer is used as a sensing element. E. G. CUMMINS

4186. **Methods of isotopic analysis of water. I. New apparatus for the drop method of measuring density.** A. I. Shatenshteĭn and Ya. M. Varshavskiĭ (L. Ya. Karpov Phys.-chem. Inst., Moscow). *Zhur. Anal. Khim.*, 1956, **11** (6), 746–748.—A simple apparatus for measuring the density of < 0·1 ml of water is described. G. S. SMITH

4187. **The free-piston burette. A new burette of high accuracy.** I. C. P. Smith (Explosives Res. and Development Estab., Min. of Supply, Waltham Abbey, England). *Chem. & Ind.*, 1957, (33), 1117–1119.—An accuracy of 1 pt. in 5000 is claimed for the 50-ml burette described, which has a free-running piston at the top of the fluid to improve reading accuracy. The burette is made of a precision-bore tube, engraved with a linear scale, which allows for the liquid retained on the walls above the piston. The piston is made from glass tubing, sealed at both ends, and made a close sliding fit in the burette tube. Its specific gravity is arranged to coincide with that of the solution on which it is to be used. It is unnecessary to engrave the burette scale all round the tube as the piston can be used to obtain readings free from parallax errors: either the top of the piston can be ground flat, perpendicular to its axis, and, if required, emphasised by a thin layer of vitreous enamel, or a single line, or a vernier scale can be engraved round the side of the piston. This system lends itself readily to automatic zeroing devices, and is also valuable when the liquid used is susceptible to contamination by, for example, O or CO_2.

J. F. P. H. GREENE

4188. **An apparatus for multiple extractions. A modification of the Kumagawa and Soxhlet apparatus.** –. Kiger. *Ann. Falsif.*, 1957, **50**, 162–166.—Details are given of an apparatus that combines the principles of the Kumagawa and Soxhlet extractors. The extraction flask and vertical condenser are standard fittings, while the central chamber is interchangeable to allow for either hot or cold extraction of the sample. The chamber usual in the Soxhlet method is modified by having a tap in the siphon tube at the side, and another tap joined at the bottom of the chamber. These taps, after removal of the sample, allow for the recovery of the solvent without dismantling the apparatus. D. G. FORBES

4189. **Semi-micro method of fat extraction.** P. Wix and J. W. Hopton (Dept. of Agric. Sci., Univ. of Nottingham, Loughborough, Leics.). *Chem. & Ind.*, 1957, (25), 805–807.—An inexpensive apparatus in which 24 samples may be assayed at one time is described and illustrated. E. G. CUMMINS

4190. **The use of the method of countercurrent partition. I. Simple rational construction of an elementary cell for a countercurrent partition apparatus.** A. S. Khokhlov and V. M. Baĭkina (All-Union Sci. Res. Inst. of Antibiotics, Moscow). *Zhur. Anal. Khim.*, 1956, **11** (6), 651–657.—A unit cell for extractions with immiscible solvents that is suitable as a member of a communicating bank of such cells for countercurrent partition is described. With a const. vol. (10 ml) of the heavier phase a rotation of the apparatus through 140° separates this from the lighter phase, which runs automatically into the next unit cell when the apparatus is returned to its original position. Each unit cell has a side tube from which liquid can be withdrawn for test as desired. G. S. SMITH

4191. **Distillation apparatus for moisture determination.** T. Barr and J. I. Yarwood (Brit. Hat and Allied Feltmakers Ass., Droylsden, Manchester). *Chem. & Ind.*, 1957, (25), 803–805.—A modification of Tryon's apparatus (*cf. J. Res. Nat. Bur. Stand.*, 1950, **45**, 362) is described and its accuracy is compared with a standard 10-ml Dean and Stark apparatus, siloxane coated. The application of this type of coating is described. E. G. CUMMINS

4192. **Testing of a rotary concentric-tube distilling column.** B. J. Mair, N. C. Krouskop and F. D. Rossini (Petroleum Res. Lab., Carnegie Inst. of Technol., Pittsburgh, Pa., U.S.A.). *Anal. Chem.*, 1957, **29** (7), 1065–1068.—A laboratory column with rotor 60 in. × 4·811 in. and annular space 0·0465 in. has been tested at speeds up to 4000 r.p.m. and power input to the pot between 200 and 400 W. The apparatus and methods of testing are described, 2:2:4-trimethylpentane being used for tests of throughput, and mixtures of this with methyl*cyclo*hexane for tests of separating efficiency. The various observed relationships between power input, theoretical plates, heat generated in rectifying section, throughput, pressure drop, and speed of rotation are given, and the results are compared with those from a smaller, highly efficient column previously described (Willingham *et al.*, *Ind. Eng. Chem.*, 1947, **39**, 706). For speeds up to 2400 r.p.m. the present results confirm those from the smaller column (20 in. × 2·93 in.), but at higher speeds the separating efficiency is much less than expected, this being ascribed to the generation of heat by turbulence in the gas phase, and it is suggested that under the given conditions a peripheral speed > 1600 cm per sec. produces more heat in this way than can be dissipated without adversely affecting the separating efficiency. R. E. Essery

4193. **Improved receiving assembly and pot closure for laboratory distilling columns.** N. C. Krouskop (Carnegie Inst. Technol., Pittsburgh, Pa., U.S.A.). *Anal. Chem.*, 1957, **29** (6), 986–987.—In the improved assembly (illustrated), a modified diaphragm valve is used instead of the usual high-vacuum glass stopcocks; this gives a leak-proof system without the use of any type of lubricant, so that contamination is avoided. The modified pot closure is fabricated from stainless steel or Monel metal, and is used instead of the usual lubricated ground glass cap. A specially treated alcohol- and hydrocarbon-resistant O-ring is another feature of the assembly. G. P. Cook

4194. **Precise-volume fraction collector.** D. N. Eggenberger and E. F. Cavanaugh (Research Div., Armour & Co., Chicago, Ill., U.S.A.). *Anal. Chem.*, 1957, **29** (7), 1116.—The collector is designed to deliver small vol. of aq. soln. from a chromatographic column to an accuracy of 0·1%. The measuring device is a small glass tube, with an outlet of Trygon or rubber tubing, pinched tight by a clamp which can be opened by a solenoid. When the soln. delivered from the column makes electrical connection between a sealed-in lower and an adjustable upper contact the clamp opens and the tube drains. A delay relay holds the solenoid open for 5 sec., and provision is made for variations is conductance of the soln. being collected and for dealing with accidental overfilling of the measuring tube. A circuit diagram shows the lay-out for operation of the turntable and measuring device, and a second diagram deals with a method for automatic changing of the temperature of the column-jacket during a run, using pre-set thermo-regulators, actuated by means of a short metal sleeve on the tube at which the change is required. R. E. Essery

4195. **Time controls for Schroeder, and Corey and Gilson, fraction collectors.** E. A. Talley and T. J. Fitzpatrick (U.S. Dept. Agric., Philadelphia, Pa., U.S.A.). *Anal. Chem.*, 1957, **29** (6), 988.—Simple changes in the designs of two fraction collectors, to remedy difficulties encountered in their practical operation, are given. K. A. Proctor

4196. **Simple arrangement of automatic apparatus for the collection of liquid fractions (laboratory note).** C. Moreau and G. Rodier (Lab. de Chimie I, Fac. des Sciences de Paris, 12 rue Cuvier). *Bull. Soc. Chim. France*, 1956, (8–9), 1253–1254.—The equipment described is intended for use where the employment of more complex apparatus is not justified. One hundred tubes, each of 50 ml, arranged on a fixed circular platform, are fed by a siphon tube attached to a rotating arm. The siphon is arranged to draw off a fixed quantity of liquid with a good degree of reproducibility. The rotation of the arm is brought about by a 'step-by-step' motor, which is controlled, through intermediate relays, by signals from a photoconductive cell. This cell is energised by a tapping from the motor supply, and its output is controlled by the variations in the light received from a lamp as the variations in liquid level in the siphon system cause the meniscus to pass between the lamp and the cell. A circuit diagram and a full description of the motor control system are given. J. F. P. H. Greene

4197. **Influence of the thickness of the adsorption layer on the potential of the micro-element used in chromatography.** B. Kamieński and I. Kulawik (Inst. Phys. Chem., Polish Acad. Sci.). *Bull. Acad. Polon. Sci.*, 1956, **4** (6), 387–391 (in English).—Further details of the preparation of the micro-element described in former papers are given. There is an optimum thickness for the layer of titanic acid gel on the antimony wire that forms the core of the electrode, but there is a fairly wide tolerance for this optimum thickness, so that the preparation of such electrodes does not present any serious problem. The method consists in simple evaporation of two drops successively of the solution on the wire. The findings are supported by curves showing electrode potential plotted against time, for electrodes with different gel thicknesses exposed to acid and base vapours. J. F. P. H. Greene

4198. **Versatile gas - liquid partition chromatography apparatus.** G. K. Ashbury, A. J. Davies and J. W. Drinkwater (Shell Research Ltd., Chester, England). *Anal. Chem.*, 1957, **29** (6), 918–925.—The apparatus is designed to incorporate future developments with the min. of modification. Functional units can be changed without affecting others and one recorder is connected to several column-furnace units. The column and column temp. can be changed rapidly. Samples of high mol. wt. can be resolved with a hot-wire conductivity-detector capable of operation up to 300°. K. A. Proctor

4199. **A moving-paper collector for column chromatography.** E. A. Bell (Dept. of Biochem., King's College, London). *Nature*, 1957, **180**, 190–191.—Individual drops of eluate are collected on a moving strip of filter-paper, propelled at constant speed by a kymograph motor and drum. The paper may then be passed through a reagent trough and between the cells of a photo-electric scanner. G. S. Roberts

4200. **Liquid sample inlet system for gas chromatographs.** R. E. Davis and J. M. McCrea (The M. W. Kellogg Co., Jersey City, U.S.A.). *Anal. Chem.*, 1957, **29** (7), 1114–1115.—The system is an adaptation of a standard mass-spectrometer liquid-inlet system and utilises an evacuated chamber with mercury-sealed orifice, appropriate means for by-passing and sweeping out the sample chamber with carrier gas, and capillary pipettes for measuring and transferring the liquid samples. The repeatability of the method is such that the coefficient of variation of peak height was 1·2% for 2-methylbutane (8 measurements) and 2·2% for 2:2:4-trimethylpentane (8 measurements), but as these estimates include other errors the sampling error may be smaller than the figures given.

K. A. PROCTOR

4201. **Head regulator for cut-off valve.** L. Bean (Nat. Bureau of Standards, Washington, D.C., U.S.A.). *Anal. Chem.*, 1957, **29** (6), 987.—The automatic cut-off valve described by Hewitt (*Anal. Chem.*, 1955, **27**, 865) for ion-exchange columns has been modified to maintain a constant head above the column at all times. K. A. PROCTOR

4202. **Apparatus for viscosity determinations.** W. Cooper and R. K. Smith (Dunlop Res. Centre, Birmingham). *Chem. & Ind.*, 1957, (27), 936–937.—Capillary viscosity-tubes need elaborate clamps resistant to water to maintain them at a correct, constant angle. A simpler assembly is suggested comprising a duralumin sleeve into which is fitted a cork containing the capillary tubes embedded in sealing wax. This sleeve fits into a holder attached to a base plate covering the thermostat bath. Heat must be avoided when cleaning the tubes, and a system of drawing solvents through the tubes, finally drying with a current of filtered air, is recommended.

F. J. M.

See also Abstracts 3990, 4021.

Optical

4203. **Industrial spectral analysis by the use of a direct-reading apparatus.** H. Bückert. *Metall*, 1956, **10** (17–18), 813–818.—Accurate analysis in two minutes is discussed. Two new instruments, a curved and a flat grating type, both having electronically smoothed spark generation, are described, and the factors influencing choice are detailed. E. G. CUMMINS

4204. **Production control Quantometer for steelworks analysis.** D. Manterfield and W. S. Sykes (Steel, Peech & Tozer, Sheffield). *J. Iron St. Inst.*, 1957, **185** (1), 105–113.—In the instrument described, the photo-currents charge condensers and the charges are related to the element content. Iron is used as an internal standard for steel analysis, and the instrument is calibrated against standard samples of known composition. Results obtained on residual elements, and low- and high-alloy concn. are equal in accuracy to those obtained by chemical methods, and the speed of analysis gives strict control over steelmaking. The instrument is intended also for use in the analysis of sinters and slags after completion of an appropriate research programme. J. O. LAY

4205. **Reference wavelengths for calibrating prism spectrometers.** E. K. Plyler, L. R. Blaine and M. Nowak (Nat. Bur. of Standards, Washington, D.C., U.S.A.). *J. Res. Nat. Bur. Stand.*, 1957, **58** (4), 195–200.—Standard wavelengths for calibrating low-resolution i.r. prism instruments have been determined from the absorption bands of polystyrene, 1:2:4-trichlorobenzene, toluene, didymium glass, and the 3·3-μ band of methane (27 rotational lines). The wavelengths listed range from 0·6 to 24 μ with most in the 3 to 6-μ region; 11 spectra are shown and the calibrated values are marked thereon. The accuracy of measurement varies from $\pm$ 0·0002 to $\pm$ 0·005 μ.

W. J. BAKER

4206. **Improvements in or relating to spectrometers.** G. Touvet. Brit. Pat. 774,476; date appl. 22.4.53. Addn. to Brit. Pat. 774,473.—The method described previously (*cf. Anal. Abstr.*, 1957, **4**, 3795) is adapted for the study of emission spectra by using the gas or vapour to be examined as the filling for the optical source or by arranging for the electrodes of the tube to be composed of the material under test. J. M. JACOBS

4207. **Interpreting device for spectral analysis.** T. Török (Inst. Inorg. and Anal. Chem., Eötvös Univ., Budapest). *Acta Chim. Acad. Sci. Hung.*, 1957, **10** (4), 357–367 (in German).—An easily constructed apparatus facilitates the conversion of photographically recorded spectral line intensities into concn. values by means of a modified three-line method. It consists of a board carrying two movable parallel scales representing log c and ΔP and a long rotating cursor. G. BURGER

4208. **Automatic long-path ultra-violet spectrometer for determination of ozone in the atmosphere.** N. A. Renzetti (Air Pollution Foundation, Los Angeles, Calif., U.S.A.). *Anal. Chem.*, 1957, **29** (6), 869–874.—A u.v. spectrometer, adapted for continuous automatic operation, has been constructed to measure the ozone concn. in air between 0 and 100 parts per hundred million (by vol.). A 300-ft. path-length is used and the concn. of ozone is derived from the absorption at 265, 280 and 313 mμ.

K. A. PROCTOR

4209. **Rapid and accurate titrations with a convenient and compact automatic derivative spectrophotometric titrator.** H. V. Malmstadt and D. A. Vassallo (Univ. of Illinois, Urbana, U.S.A.). *Anal. Chim. Acta*, 1957, **16** (5), 455–463.—A stirred titration vessel is set in the light path between a 6-V tungsten-filament lamp and a barrier-layer cell. The cell and the burette valve are connected to a Sargent-Malmstadt derivative control unit (*cf. Anal. Abstr.*, 1957, **4**, 763). The assembly is used for several titrations that give a colour change at the end-point. W. C. JOHNSON

4210. **Salvaging of silver chloride windows.** W. C. Schwemer, J. E. Murphy and L. Williamson (S. C. Johnson & Son, Inc., Racine, Wis., U.S.A.). *Anal. Chem.*, 1957, **29** (7), 1113.—Scratched and darkened silver chloride plates can be restored to their original transparency by first removing foreign material by scraping the surface with a single-edge razor blade and then sanding with a wet-dry sandpaper of suitable coarseness. The window is

then immersed for 2 min. in conc. aq. NH_3, rinsed with water and dried with a lint-less cloth. Scratches are then removed by pressing at 8000 p.s.i. in a polished, chrome-surfaced die such as is used in forming potassium bromide discs.

K. A. PROCTOR

Thermal

4211. **High-temperature laboratory furnace.** H. Forestier and A. Mangin (Inst. de Chimie, Fac. des Sciences, Strasbourg). *Bull. Soc. Chim. France*, 1956, (8–9), 1200–1202.—The furnace described was designed for studying the reactions of metal oxides at high temperatures. The sample can be heated *in vacuo* or under controlled atmospheres of inert or reducing gases. The heating element is a tungsten resistor. This type of element was chosen in preference to other possible systems for the following reasons—(*i*) the amount of heat developed is independent of the material being heated; (*ii*) thermal stability is good; (*iii*) heat distribution in the central zone of the furnace is good; (*iv*) good protection against contamination can be provided; and finally (*v*) for equal heating properties, such a furnace is more robust, cheaper, and easier to instal than other types. A full description of the construction is given, with a sectioned drawing, and details are also given of the power supply, consisting of a tapped autotransformer feeding the furnace through a step-down transformer. The input voltage is 380 V, single phase, 50 c/s, and the output 0 to 15 V, with a maximum power output of 40 kVA. At 2000° the power consumption is 17 kVA, which can be reached in 30 seconds.

J. F. P. H. GREENE

4212. **Studies in the properties of capillary-held liquids. I. Apparatus for determining freezing- and boiling-points of capillary condensates.** B. R. Puri and Y. P. Myer (Dept. of Chem., Punjab Univ., Hoshiarpur). *J. Sci. Ind. Res., B, India*, 1957, **16** (2), 52–57.—The apparatus is described, and results are quoted for benzene and H_2O adsorbed on silica gel and bentonite at different relative vapour pressures.

C. A. SLATER

4213. **A recording vacuum thermobalance.** J. G. Hooley (Dept. of Chemistry, Univ. of British Columbia, Vancouver, B.C.). *Canad. J. Chem.*, 1957, **35** (4), 374–380.—A recording thermobalance is described on which changes of weight of up to 1000 mg can be followed for samples of up to 10 g. The balance is so designed that it can be operated under pressure or vacuum, and during heating or cooling of the sample. Basically the instrument is a conventional quartz-spring balance, in which a quartz-enveloped steel rod is interposed between the spring and the pan. The whole is enclosed in a pressure-tight system, and thermostatically controlled water is circulated round the spring tube. The windings of a transformer, whose core is the steel rod, surround the system at the level of the rod; adjustment and correction for temperature variations can be made in the transformer mounts. A 6·3-V a.c. supply feeds the primary of the transformer, whose output is amplified, rectified, and used to provide a signal to a precision millivolt recorder. Reproducibility of $\pm$ 1 mV for day-to-day operation is claimed; the millivolt to weight-change relationship is found to be linear up to a transformer core movement of 0·2 cm, and the sensitivity of the instrument described is about 20 mV per mg. Equipment for weighing larger samples could be made by using less sensitive springs, and the design could be adapted for the measurement of dimensional changes, with a sensitivity of at least 2000 mV per mm.

J. F. P. H. GREENE

4214. **Apparatus for measuring gas in molten metals.** R. M. Boehme and R. B. Lawrance (Nat. Res. Corp.). U.S. Pat. 2,795,132; date appl. 25.3.55.—The invention relates to a vacuum hot-extraction type apparatus for determining hydrogen in metals and alloys.

LIGHT METALS BULL. ABSTR.

Electrical

4215. **Apparatus for continuous paper electrophoresis.** G. L. Selden and U. Westphal (Army Med. Res. Lab., Fort Knox, Ky., U.S.A.). *J. Lab. Clin. Med.*, 1957, **49** (5), 786–792.—The apparatus described comprises a plastics cabinet divided into an upper separation chamber and a lower collection chamber. Separation is on specially cut Whatman No. 3 paper (35 cm $\times$ 47 cm) to which the sample is applied by a motor-driven syringe. Provisions are made for a downward flow of buffer, the application of a homogeneous electric field, and for efficient removal of the separated products. The continuous separation of normal human serum proteins is described.

W. H. C. SHAW

4216. **Anodic stripping polarography.** J. G. Nikelly and W. D. Cooke (Baker Lab., Cornell Univ., Ithaca, N.Y., U.S.A.). *Anal. Chem.*, 1957, **29** (6), 933–939.—In this method of analysis a metal was deposited on an electrode and anodically removed under controlled conditions; it was possible to detect metal ions at concn. as low as 10^{-4} μg per ml and to determine Pb and Cd in spectrographically pure zinc. No pre-treatment was necessary for a small mercury electrode, and no change in calibration values was observed over a period of 8 months. Half-wave potentials are independent of concn. and agree closely with the half-wave potentials obtained at a dropping mercury electrode. The method is applicable only to metals which can be deposited in mercury and anodically removed. The precision of the method is $\simeq$ 4%.

K. A. PROCTOR

4217. **Efficient removal of dissolved oxygen in polarography.** K. Koyama and C. E. Michelson (General Electric Co., Richland, Wash., U.S.A.). *Anal. Chem.*, 1957, **29** (7), 1115–1116.—Methods of removing dissolved oxygen from a solution before polarography have been examined and compared.

K. A. PROCTOR

4218. **Reference electrode for making pH measurements.** Canadian Aviation Electronics Ltd. [Inventor: O. V. Ingruber]. Brit. Pat. 770,597; date appl. 3.6.55.—The reference electrode is designed to give satisfactory and reproducible results at temp. >160° and pressures >120 lb per sq. in. It comprises a stem with its upper portion, which is surrounded by a cooling jacket, flared outwards and fused to the lower end of a body section containing a calomel half-cell which is connected in a pH-measuring circuit. The stem contains a saturated soln. of KCl as liquid electrolyte, and also layers of KCl crystals alternating with layers of insol. material, *e.g.*, splinters of crushed glass, glass beads

or asbestos. The upper end of the stem is plugged with fibrous material (clean cellulose fibres) with a small amount of KCl on top to maintain saturation.
J. M. JACOBS

4219. **A 250-megacycle high-frequency titrimeter.** E. S. Lane (A.E.R.E., Harwell, England). *Analyst*, 1957, **82**, 406–415.—A stable high-frequency titrimeter operating at 250 Mc/s is described and illustrated with examples of its application to acid - base and argentimetric titrations, titrations in non-aq. solvents, determination of K by direct titration with Na tetraphenylboron, and amperometric titrations. A. O. JONES

4220. **Analytical applications of zirconium electrode.** S. Megregian (Dept. of Health, Educ. and Welfare, Washington, D.C., U.S.A.). *Anal. Chem.*, 1957, **29** (7), 1063–1065.—A study of the zirconium electrode in soln. of F^- shows that the current is proportional to the concn. of F^- between 2·5 and 20·0 mg per litre. At constant acidity Zr can be titrated with F^-, but F^- cannot be titrated directly with zirconium soln. The determinations can be performed in less than 30 min., and the apparatus required is simple to assemble. K. A. PROCTOR

4221. **Coulometric titration.** D. D. DeFord and J. N. Pitts, jun. (to Research Corp.). U.S. Pat. 2,744,061; date appl. 1.5.56.—An indirect coulometric titration method and apparatus are described. The titration reaction occurs in a vessel separate from the electrolytic cell in which the titrating reagent, an electrolyte component of a reagent soln., is formed. The method is applicable to acid - base titrations as well as those requiring I, Br, Cl, Cu^+ and Fe^{2+}. The g milli-equiv. in the unknown are calculated by multiplying the average current (amp.) flowing through the cell by the time (sec.) to read an indicator end-point and dividing by the constant 96·5. CHEM. ABSTR.

4222. **Pulse coulometry.** M. A. V. Devanathan and Q. Fernando (Dept. of Chem., Univ. of Ceylon, Colombo). *Trans. Faraday Soc.*, 1956, **52**, 1332–1337.—A coulometer is described in which current pulses of const. magnitude are used, the number of which can be electromechanically recorded. The pulses are generated with an Abraham and Bloch multivibrator. This coulometer can be used for the titration of 100 to 400 μg of oxine (in 0·1 *N* HCl and aq. 0·5 *N* NaBr) with electrolytically generated Br. Provided that the number of pulses exceeds 200, the error is $< 1\%$. The procedure is described. The rate at which the micro-ammeter needle returns to zero when the current is switched off decreases near the end-point; once this point is passed there is a permanent deflection up to a max. of $\simeq 15$ μA. The end-point is located by extrapolation on a linear plot of μA *vs.* number of pulses. The pulse coulometer should be calibrated for each type of titration. W. J. BAKER

4223. **High stability nuclear magnetic resonance spectrograph.** E. B. Baker and L. W. Burd (Dow Chemical Co., Midland, Michigan, U.S.A.). *Rev. Sci. Instrum.*, 1957, **28** (5), 313–321.—The authors describe improvements to N.M.R. circuitry designed to permit the use of electromagnets giving higher field strength than is possible with permanent magnets, although the actual field strengths used are not reported. The improvements consist in providing stabilisation, controlled by an error signal from a reference sample, to compensate for both long- and short-term supply variations, and for oscillator instability. They have been achieved by fairly simple modifications of commercially available equipment. The principle of operation is the provision of a stabilising signal from the scanning (by a frequency sweep) of a reference sample simultaneously with the test sample. The test and reference sample circuits are generally similar. Calibration is provided by an advance run-through on the appropriate frequency range with the reference sample (generally water), and scale expansion without loss of accuracy with regard to the reference sample is possible. Preservation of the basic field to frequency relationship (Larmor relation) is brought about by varying frequency rather than field, as in this way it is simpler to reduce time lag. Suppressed carrier technique is used, with the selected side band fed to the test and reference samples: that fed to the test sample is swept automatically in relation to the other; the frequency of the audio signal in the reference section is manually variable, and the R.F. carrier is common to both circuits. J. F. P. H. GREENE

See also Abstract 3833.

ABBREVIATIONS

Certain abbreviations in everyday use are not included in the following list. When any doubt might arise from the use of an abbreviation or symbol the word is printed in full.

alternating current	a.c.
ampere	amp.
Ångström unit	Å
anhydrous	anhyd.
approximate, -ly	approx.
aqueous	aq.
atmospher-e, -ic	atm.
boiling-point	b.p.
British thermal unit	B.Th.U.
calorie (large)	kg-cal.
calorie (small)	g-cal.
centimetre	cm
coefficient	coeff.
concentrated	conc.
concentration	concn.
constant	const.
corrected	(corr.)
crystalline / crystallised	cryst.
cubic	cu.
current density	c.d.
cycles per second	c/s
density	ρ
density, relative	d or wt. per ml
dilute	dil.
direct current	d.c.
distilled	dist.
ethylenediaminetetra-acetic acid	EDTA
electromotive force	e.m.f.
equivalent	equiv.
gram	g
gram-molecule	mole
half-wave potential	$E_{\frac{1}{2}}$
hour	hr.
hydrogen ion exponent	pH
infra-red	i.r.
insoluble	insol.
international unit	i.u.
kilogram	kg
kilovolt	kV
kilowatt	kW
liquid	liq.
maxim-um, -a	max.
melting-point	m.p.
microgram	μg (not γ)
microlitre	μl
micromole	μmole
micron	μ
milliampere	mA
milli-equivalent	milli-equiv.
milligram	mg
millilitre	ml
millimetre	mm
millimicrogram	mμg
millimolar	mM
millivolt	mV
minute (time)	min.
molar (concentration)	M
molecul-e, -ar	mol
normal (concentration)	N
optical rotation	α_λ^t
ounce	oz
parts per million	p.p.m.
per cent.	%
per cent. (vol. in vol.)	%(v/v)
per cent. (wt. in vol.)	%(w/v)
per cent. (wt. in wt.)	%(w/w)
potential difference	p.d.
precipitate (as a noun)	ppt.
precipitated	pptd.
precipitating	pptg.
precipitation	pptn.
preparation	prep.
qualitative, -ly	qual.
quantitative, -ly	quant.
recrystallised	recryst.
refractive index	n_λ^t
relative band speed	R_{F}
relative humidity	r.h.
revolutions per minute	r.p.m.
saponification value	sap. val.
saturated calomel electrode	S.C.E.
second (time)	sec.
soluble	sol.
solution	soln.
specific gravity	sp. gr.
specific rotation	$[\alpha]_\lambda^t$
square centimetre	sq. cm
standard temp. and pressure	s.t.p.
temperature	temp.
ultra-violet	u.v.
vapour density	v.d.
vapour pressure	v.p.
volt	V
volume	vol.
watt	W
wavelength	λ
weight	wt.

In addition, the following symbols may be used in conjunction with numerical values or in mathematical expressions—

greater than	$>$	less than	$<$
not greater than	$\ngtr$	not less than	$\nless$
is proportional to	$\propto$	of the order of, approximately	$\simeq$

The principal Pharmacopoeias are denoted by B.P., U.S.P. or D.A.B., together with the identifying roman numeral or year.

Valency states are represented by a superscript roman numeral, *e.g.*, Fe^{II}, Mo^{V}. Substances in the ionic state are represented by Na^+, Fe^{2+}, Fe^{3+}, etc., for cations and by Cl^-, SO_4^{2-}, PO_4^{3-}, etc., for anions.

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